Watertec Engineering Pty Ltd

Information Sheet

PRINCIPLES OF OZONE GENERATION

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WHAT IS OZONE?

Ozone is the triatomic state of oxygen, that is, it is a molecule comprising of three oxygen atoms having the chemical symbol O_3. Although ozone does exist naturally, it is a relatively unstable and reactive gas. Therefore ozone exists in the lower atmosphere at low concentrations. The greatest quantities of natural ozone are found at levels of up to 6 ppm in the stratosphere, thus the term - the ozone layer. Natural production of ozone is by either UV radiation or lightning.

The Dutch scientist Van Mauren first reported the recognition of ozone in 1785 whilst he was experimenting with a powerful electrical machine. The following years led to more reported instances of ozone production during work with electrical discharges and electrolysis. By 1867 the identity and structure of ozone was confirmed with scientists looking towards its usefulness.

As well as being a powerful disinfectant, today ozone is the strongest commercially available oxidant and as such has a vast array of applications. Most commonly these have been water treatment for many different industries, and effluent treatment.

METHODS OF PRODUCTION

As a commercially demanded treatment, there have been years of research and development put into methods of ozone production. Today there are four recognised methods:

1. Corona Discharge
2. Ultraviolet Radiation
3. Electrolysis
4. Radiochemical

Any method of generating ozone relies on applied energy to break the bonds holding the oxygen atoms in a molecular form, allowing them to dissociate and then re-form as ozone.

The applied energy is random in its action, resulting in a high level of friction in the reaction process. For this reason ozone production is inefficient, and is accompanied by a large percentage of waste heat.

1. Corona Discharge

Corona discharge is the condition created when a high voltage passes through an air gap. In the case of ozone production, this high voltage transfers energy for the breaking of the O_2 molecule, allowing the formation of a 3-atom oxygen molecule - ozone. This method is today the most widely used for commercial ozone production.

2. Ultraviolet Radiation

As indicated, the formation of ozone from oxygen is endothermic, that is it requires energy. When exposed to light an oxygen molecule in a ground state will absorb the light energy and dissociate to a degree dependent on the energy and the particular wavelength of the absorbed light. The oxygen atoms then react with other oxygen molecules to form ozone.

Each wavelength of light favours different reactions and their quantum yield. The breakdown of the oxygen molecule has a higher yield at wavelengths less than 200nm. However just as oxygen absorbs light, so does ozone. The dissociation or photolysis of ozone has its greatest yield between 200 and 308nm. The following graph highlights the fact that the wavelength of UV light used for specific disinfection (254nm) is in the peak wavelength range for ozone destruction.

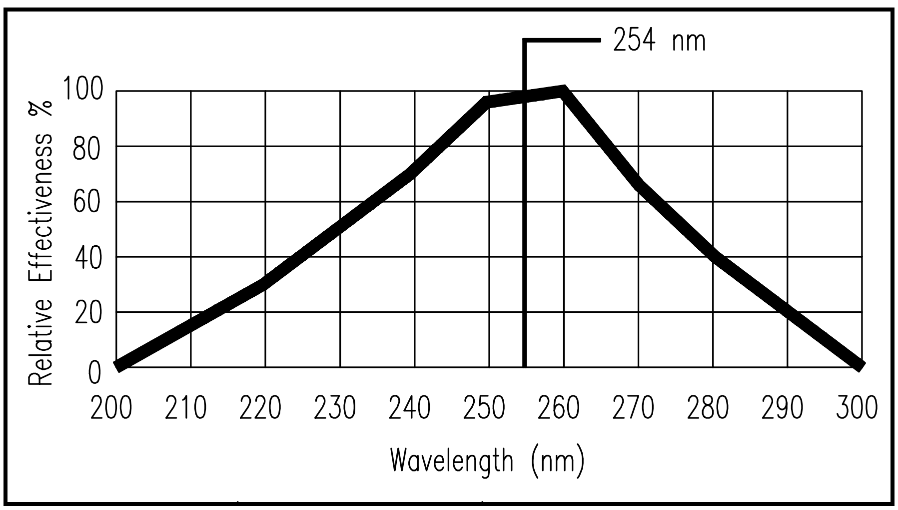

Figure 1. UV Destruction of Ozone

For effective ozone production it is therefore necessary to utilize a short wavelength ~185nm. In theory, the yield of O_3 from 185nm UV light is 130g/kWh of light. As lamp efficiencies are so low, ~1%, the production per kWh from the power source is greatly reduced.

In practice, with the present state of development, UV lamps can only produce about $20gO_3$/kWh of ozone when using oxygen as the feed gas. However, they are more commonly used with vacuum injection systems drawing atmospheric air over a UV lamp tube, and generate 1-$2gO_3$/kWh in concentrations of 0.1% w/w of air. These are very simple in design, require no air preparation and are ideal for small applications such as small fishponds, laboratory work, and odour elimination.

3. Electrolysis

Electrolysis is the process in which an electric current is passed through a liquid, causing a chemical reaction, resulting in the evolution of gases. In relation to ozone production, water can be used as the electrolyte leading to direct diffusion, or special electrolytes such as H_2SO_4 can be used and ozone gas drawn off and diffused and contacted by the usual methods.

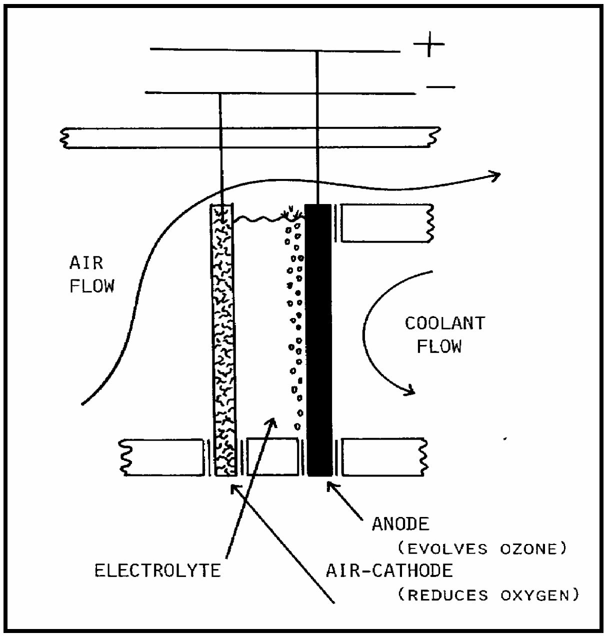

Figure 2. Electrolytic Ozone Generator Cell Design

Work has been done with different electrolytes and anode materials to improve the efficiency of production and minimise the corrosive reactions on the anode surface. The concentration of ozone produced is determined by the current density acting on the cell. With the use of an ozone gas evolving cell as depicted in this diagram, high concentrations of ozone, at least 10% can be achieved. The use of electrolysis for ozone production is presently limited to small units used for applications that require high concentrations of ozone, and in-situ diffusion of ozone into ultra pure water. Currently, whilst their capital cost is favourable compared to corona discharge units, the operating costs are significantly higher. Further development needs to be done on the composition of electrolytes and cathode/ anode manufacture before they become a commercially viable production method.

4. Radiochemical

High energy irradiation of oxygen by radioactive rays can promote the formation of ozone. Whilst high yields have been achieved under specific conditions using oxygen, the best results from an air flow through system at atmospheric pressure, has been ~ 3-4 mg/m^3. The process is fraught with complications in filtering harmful isotopes and it is not viewed with potential use in commercial applications.

OZONE PRODUCTION BY CORONA DISCHARGE

Ozone production by electrical discharges is a common occurrence by things such as photocopiers, faulty light switches, motor brushes and power transmission lines. The use of electrical power to generate ozone by corona discharge has been, and remains, the most commercially viable method. Essentially a corona is characterised by a low current electrical discharge across a gas-filled gap at a relatively high voltage gradient. This results in the gas becoming partially ionized, and taking on a diffused bluish glow when pure oxygen is used as the feed gas (the colour is more mauve when using air). As a contrast, an arc discharge is characterized by a high current density, causing a highly ionized gas and a low voltage gradient across the gap.

In essence the configuration of a typical cell is as described in the following diagram.

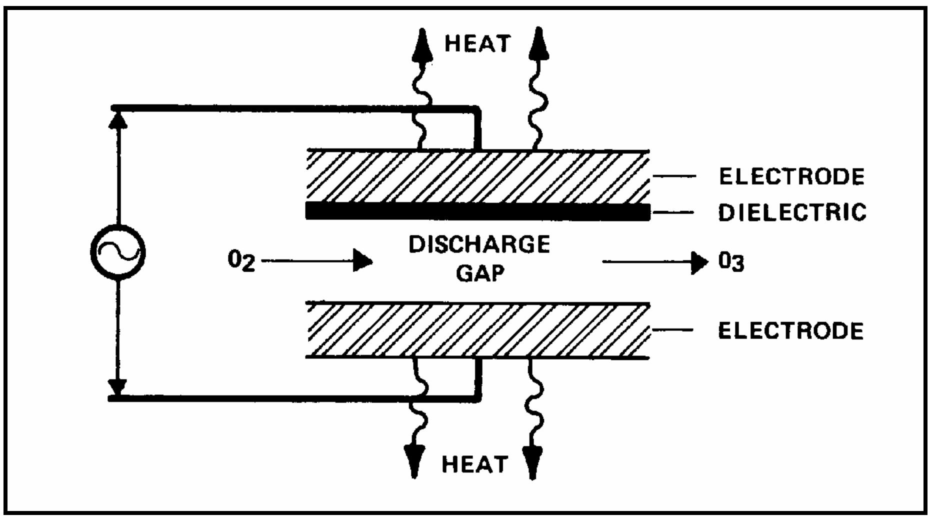

Figure 3. Corona Discharge Cell Configuration

Ozone is produced in the corona as a direct result of power dissipation in the corona. Electrons are accelerated across an air gap so as to give them sufficient energy to split the oxygen double bond, thereby producing atomic oxygen. These oxygen atoms then react with other diatomic oxygen molecules to form ozone.

$$3O_2 + ENERGY = 2O_3$$

The amount of ozone produced together with the efficiency and reliability of that production are directly related to a number of key factors the main ones being: -

1. Feed gas quality
2. Power input.
3. Generation module construction
4. Temperature.

1. Feed Gas Quality

The amount of ozone produced in a given ozonator design is relative to the concentration of oxygen in the gas feeding the corona. Basically, the more oxygen in, the more ozone out. In general, ozone concentrations of 1-3% using air, and 3-10% using oxygen can be obtained. There are, however, other complex considerations that need to be accounted for, such as air preparation.

2. Power Input

The amount of energy applied to the gas gap between the electrodes is critical to the concentration of ozone produced. It is a combination of the voltage and frequency that results in a given energy input. Typically, voltages of between 7 to 30 kV are used with frequencies ranging from mains supply of 50 or 60 Hz, medium up to 1000 Hz, and high up to 4000 Hz.

Until recently the most common design was to use mains frequency and vary the voltage. Limitations to this method include: (a) high peak voltages increase the stress on the dielectric resulting in more frequent failures, and (b) the ozone output is not linear to the change in applied voltage.

Better technology has led to the use of frequency control to vary the power input and thus ozone output. By using higher frequencies and operating at lower voltages the dielectric stress is minimised. Other benefits include an increase in generator efficiency, a linear control relationship and a greater turndown capability.

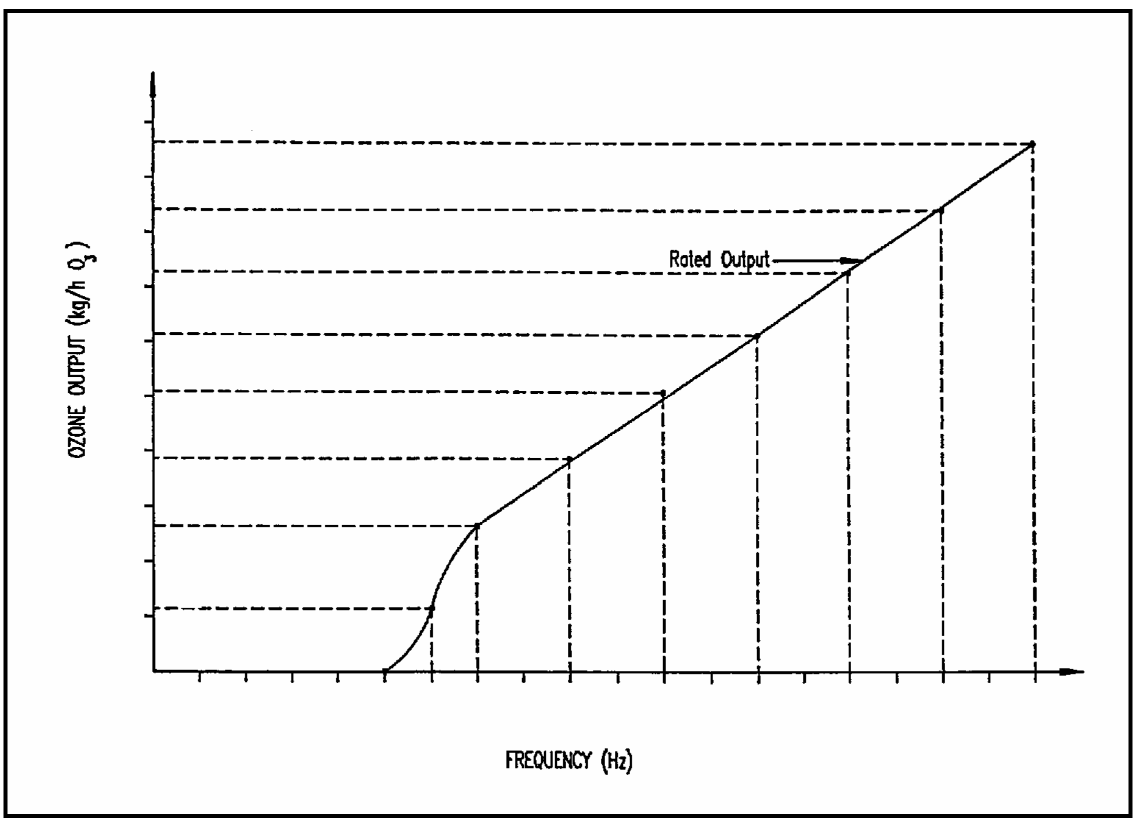

Figure 4. Typical Relationship between Frequency & Ozone Output

When designed correctly, using modern power electronics, the generator efficiency and capabilities are maximised by manipulation of all power considerations, such as voltage, frequency, current and waveform.

3. Generation Module Construction

The design of a corona discharge cell is critical to ensure maximum ozone output from given operating conditions such as power input and gas feed whilst maintaining reliable operation and long service life.

Both the materials used for module construction and the geometry in which they are configured are paramount to generator performance. It is critical that the energy dissipates evenly across and through both the entire cell gap and dielectric material to prevent any ‘hot spots’ and premature failure.

There are two basic geometric designs; parallel flat plates and concentric tubes. The flat plate generator is of two main design configurations. The Otto Plate consists of flat hollow blocks separated by two glass plates and a gas space. The cooling water flows through the hollow blocks that serve as both the electrodes and heat dissipaters. These units are designed to operate at below atmospheric pressure and therefore restricted to use with negative pressure dissolution systems.

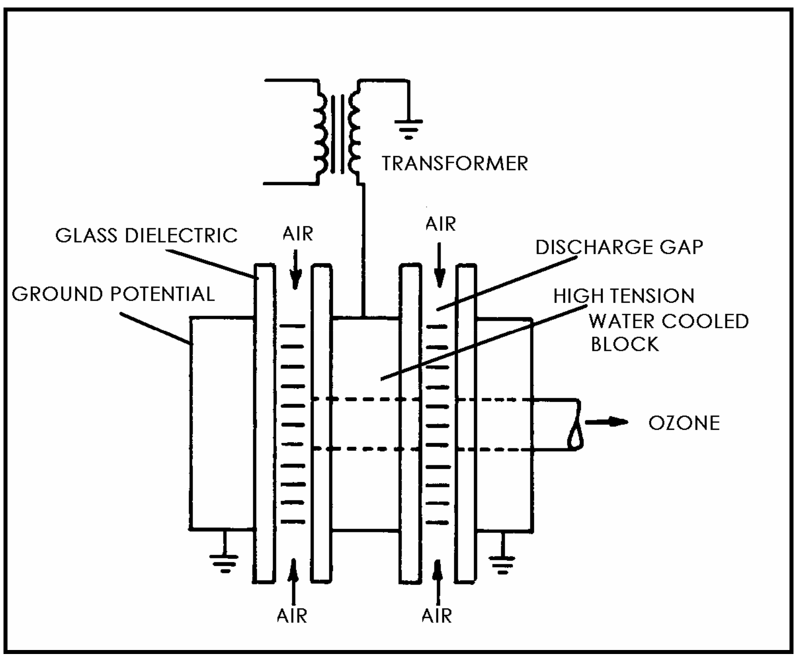

Figure 5. Otto Plate Ozone Generator Design

The Luther plate is characterised by the use of a ceramic dielectric coating on the electrodes with air being forced through aluminium heat sinks as the cooling system. These units are designed to operate at slightly positive pressure ~ 100 kPa.

The concentric tube design is the most common, and is categorised by being either a vertical or horizontal configuration. Each of these again has various configurations of tube design, airflow and electrical discharge path. In essence, the dielectric is a glass tube and the high voltage electrode is either a conductor inserted within the tube or a metallic film coating the internal surface of the tube. Typically the vertical tubes use an inner high voltage alloy electrode with an air gap to the glass dielectric, which is in direct contact with the cooling water, serving as a ground electrode. This can be as a two pass or as a flow through design.

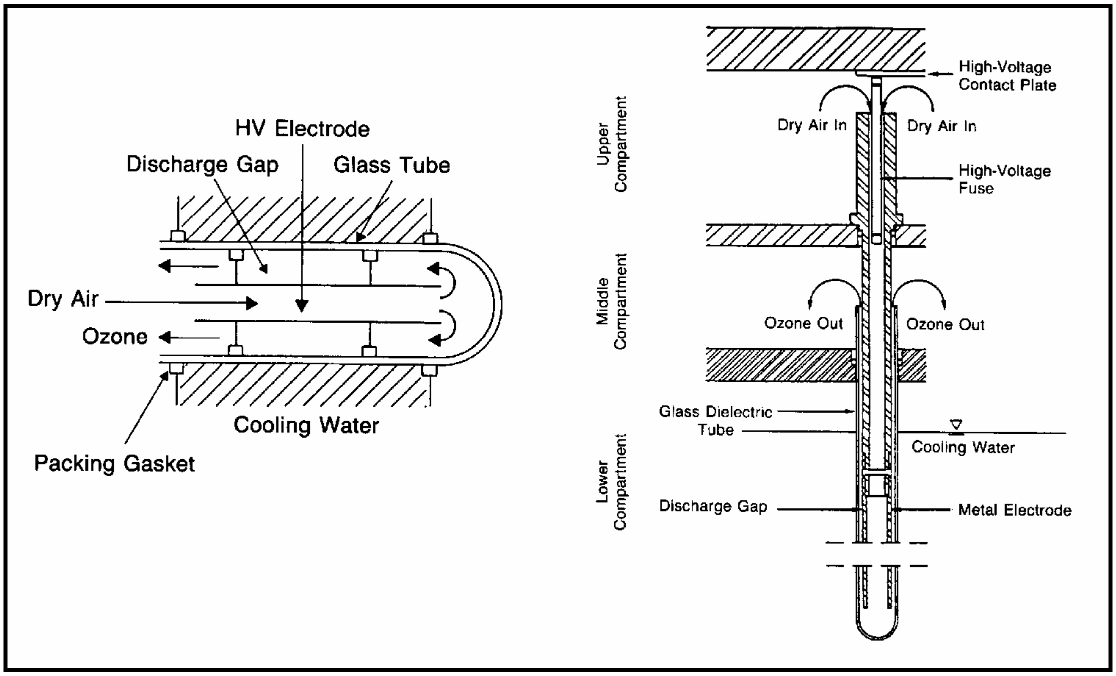

Figure 6. CD Vertical Tube Flow Within & Return Design

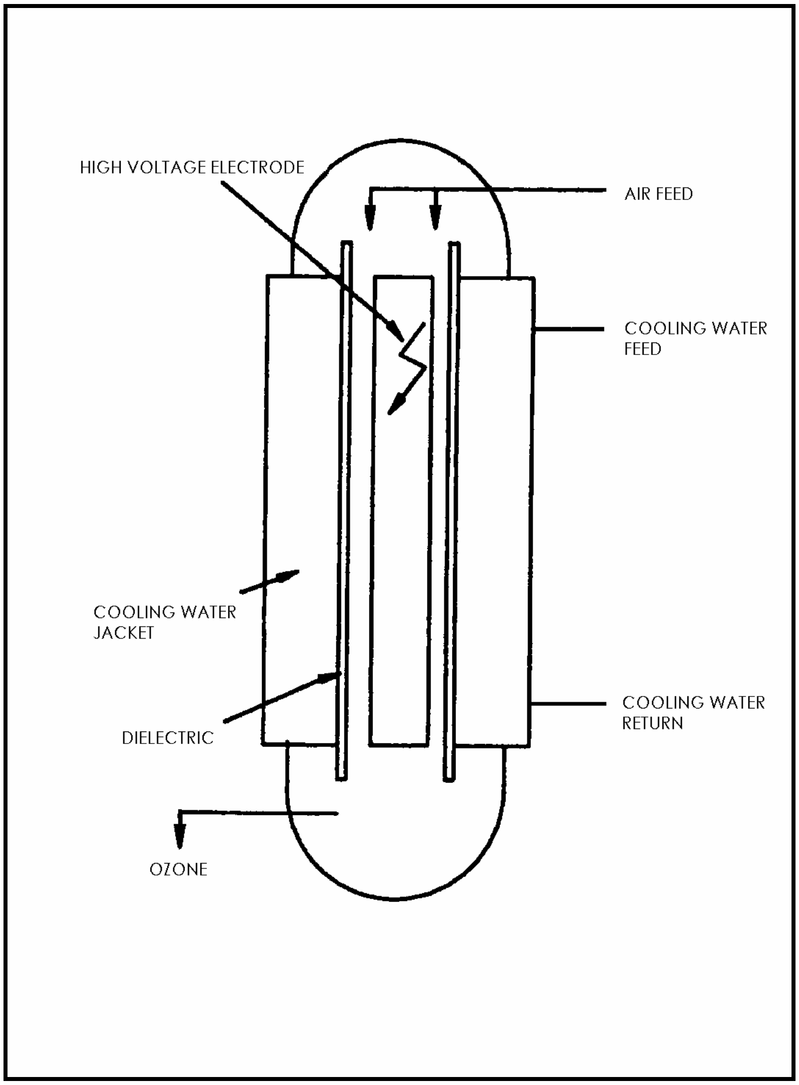

Figure 7. CD Vertical Tube Flow Through Design

These units may be designed for both vacuum or pressure feed, and are most suitable for medium ozone outputs, up to 1.5 kg/h.

The large capacity generators are of the horizontal tube type. These consist of a metallic film on the inside surface of the glass dielectric. In this case, the electrical current travels through the dielectric first, before transversing the air gap to a stainless steel water jacket serving as the ground electrode. The stress on the dielectric is greater, as it is not directly cooled as in the case with the vertical design. However, should a tube fail, a simple fusing system will allow the generator to continue operating on the remaining tubes. Failure of a vertical tube cell will flood the module with water making the generator inoperative due to a direct electrical short. Whilst a fusing system is possible, its complications are not justified.

The horizontal tubes are arranged in a honeycomb configuration into what is commonly called the ‘Iron Lung’ style of design. The largest of these units is available with a capacity over 100 kg/h.

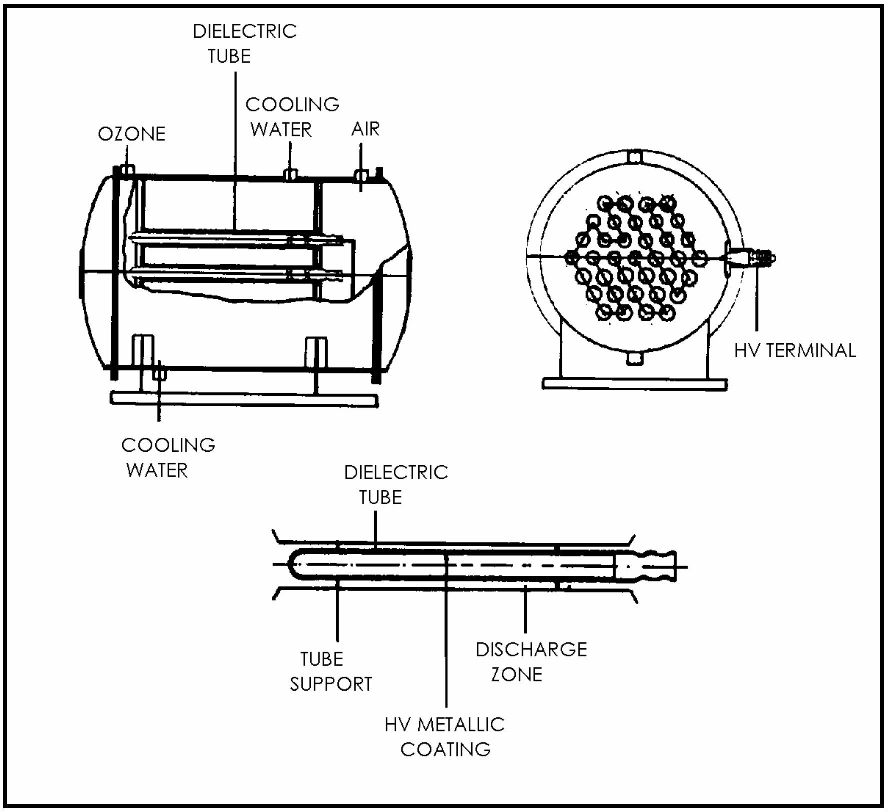

Figure 8. CD Horizontal Tube Design

There are other generator designs using a ceramic dielectric impregnated with the high voltage electrode. These usually operate at high frequencies and have often proved to be unreliable.

Material selection is critical to cell performance and reliability. Typically the dielectric material of either glass or ceramic is chosen for its high dielectric strength (V/mm) and its high dielectric constant. A good HV electrode is chosen for its ability to handle a high current density (W/cm^2), as characterised by its ability to conduct a high current per unit surface area with minimal heating.

In selecting materials and their physical dimensions, it is the balance between a highly power efficient fragile construction and a less efficient construction of robust quality that will give long term reliability.

4. Temperature

As mentioned earlier, ozone generation is an inefficient process whereby about 80% of the applied electrical energy is wasted as heat. It is essential to remove this heat as not only does it increase stress on ozonator components but ozone is destroyed at elevated temperatures. The quality and temperature of the cooling water has a major influence on the output efficiency and reliability of an ozonator.

Because the vertical tube design directly cools the dielectric, it is a more efficient cooling system than that of the horizontal type. Cooling flows of vertical designs are in the order of

1,400L/h/kg ozone produced at 20°C, whereas horizontal designs require 2 to 3 times this flow.

Double cooled vertical tube designs provide the best cooling, but pose significant maintenance problems for sealing and isolation of both electrode systems. It is therefore not a common design in practical applications.

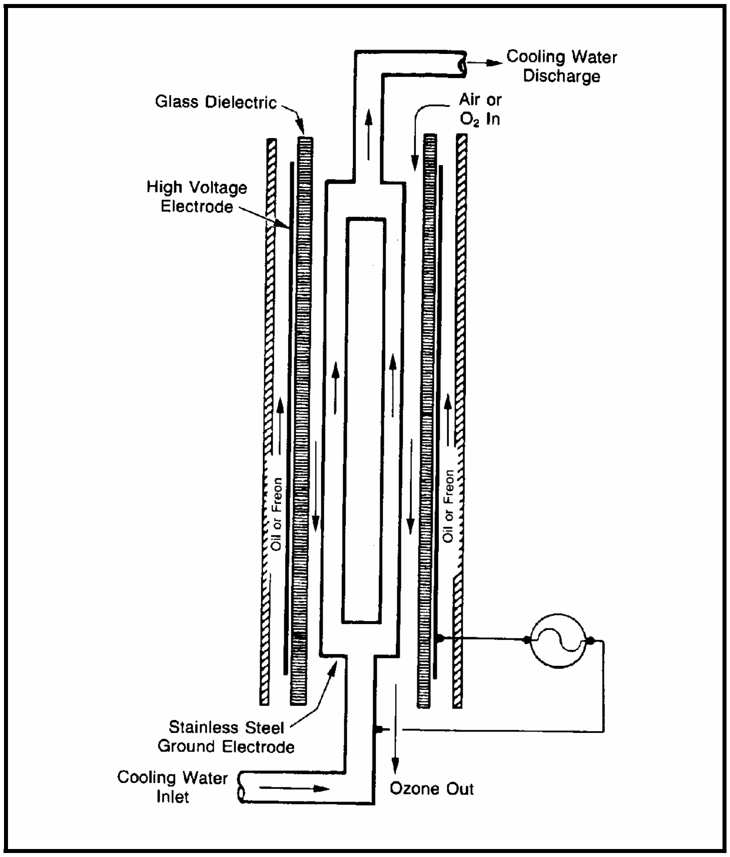

Figure 9. CD Vertical Tube Double Cooled Generator

AIR PREPARATION

Oxygen is the raw material for ozone production and can be supplied to the generator as air, high purity oxygen or a combination of both. Air feed systems are the most common, as they provide the lowest cost source of oxygen on a continuous basis. It is imperative that the supply source of oxygen is dry and free of particulate material. Typically the feed gas should have a dew point of at least -60°C and be filtered to 5 microns. Any moisture present will not only reduce the generator efficiency, but also lead to the formation of nitric acid, which causes corrosive damage to equipment and possible contamination of the treated water. Particulate material is a source of fouling to the equipment and can deposit on surfaces within the corona cell causing an increase in localised current draw and eventually failure of cell components.

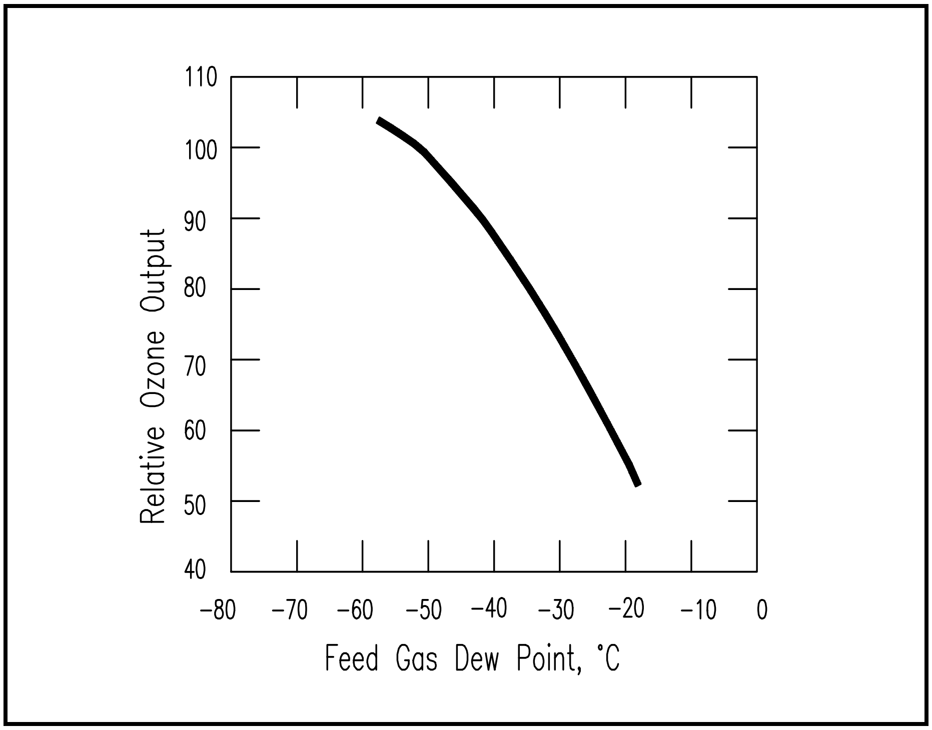

Figure 10. Effect of Water Vapour on Ozone Production

There are two common types of air preparation systems that can be characterised by their method of air drying;

1. Heatless desiccant dryer
2. Heat regenerated dryer

The heatless desiccant dryer requires pressure to drive the air through a moisture absorbent, such as molecular sieve, activated alumina, or silica gel. The dryer consists of two chambers that alternate the duty and purge phases. In general the drying system consists of the following components:

Air compressor → air receiver → 5 micron filter → refrigerated cooler → 0.01 micron coalescing filter → pressure swing desiccant dryer → 0.1 micron dust filter.

The heat regenerative dryer relies on the vacuum induced by the ozone injection system to draw air through a desiccant filled chamber that absorbs the moisture. There are usually two chambers that alternate their duty according to a timer. During the off cycle, heat is blown through the media to remove the excess moisture.

In selecting an air preparation system, consideration needs to be given to the conditions in which the generator is to operate. Such factors as ambient temperature, elevation, humidity, air born contaminants and seasonal variations are critical. Whilst it may be the less costly and simpler alternative, heat regenerative dryers are not suitable for many ozone installations, particularly in areas of high humidity. Another problem with this type of drier is that no effective filter can be installed between the drying media and ozone cell, thus allowing particles into the ozone generation zone.

Air fed generators will only efficiently produce up to 3% w/w ozone. Where greater concentrations of ozone are required, such as for advanced oxidation processes, an oxygen fed system is the answer. Because of the random bombardment of molecular oxygen by the high energy electrons, a greater concentration of oxygen in the corona will result in more ozone being produced for the same energy input. In other words, the greater the concentration of oxygen in the feed gas, the greater is the efficiency of production. The net effect is that less power is consumed to generate a given quantity of ozone as the oxygen concentration increases.

Oxygen ~ 5 to 8kW/kg   Air ~ 15 to 18kW/kg

The two common sources of high purity oxygen for gas feed are

1. Liquid oxygen (LOX).
2. On site generation by Pressure Swing Adsorption (PSA) system.

1. Liquid oxygen (LOX)

Whilst the capital cost of air preparation equipment is avoided, a LOX system incurs an ongoing consumption cost which is in the order of $0.25 to $0.50/m^3 O_2. Depending on the diffusion and contacting system, this additional operating cost may make it economically necessary to dry and recycle the off-gas back to the generator.

2. Pressure Swing Adsorption (PSA)

This system operates on a similar principle to the heatless desiccant dryer in that air is pressure fed to a molecular sieve. The media is selected such that during the high pressure phase it adsorbs nitrogen, moisture, hydrocarbons, and CO_2, leaving oxygen to flow through. When the pressure is reduced the vapour, nitrogen and other gases desorb and are removed from the vessel by the purge gas. In practice, the product gas contains about 90-95% O_2 and a few percent each of nitrogen and argon.

Other methods of on-site oxygen generation include vacuum swing adsorption and cryogenic treatment. The decision of whether to use air or oxygen as the feed gas and which particular system will be dictated by first the required ozone demand and concentration and then the relative cost of each system both as an up front capital cost and operating cost.

From a long term operating point of view, it is significant that the power cost of generating ozone from oxygen is substantially lower than generating from air.

OZONE OUTPUT CONTROL METHODS

Ozonator outputs are generally measured in g/h or pounds/day (ppd). This output can be regulated by controlling; (a) the concentration in a given gas flow by varying the applied power, or (b) keeping the concentration constant by varying both gas flow and power.

Typically, the first method is used with air fed systems, and the second is used with LOX fed systems where gas wastage needs to be minimised. As described earlier, depending on the electrical design of the generator, the power input can be manipulated by changes to voltage and/or frequency, the greatest versatility being provided with generators that control both parameters. Gas flow control is by a restriction valve on the gas output line of the generator. These control methods can be manually operated, or automated from process signals.

Three common sources of automation are;

1. Flow pacing
2. Ozone residual
3. Off-gas concentration

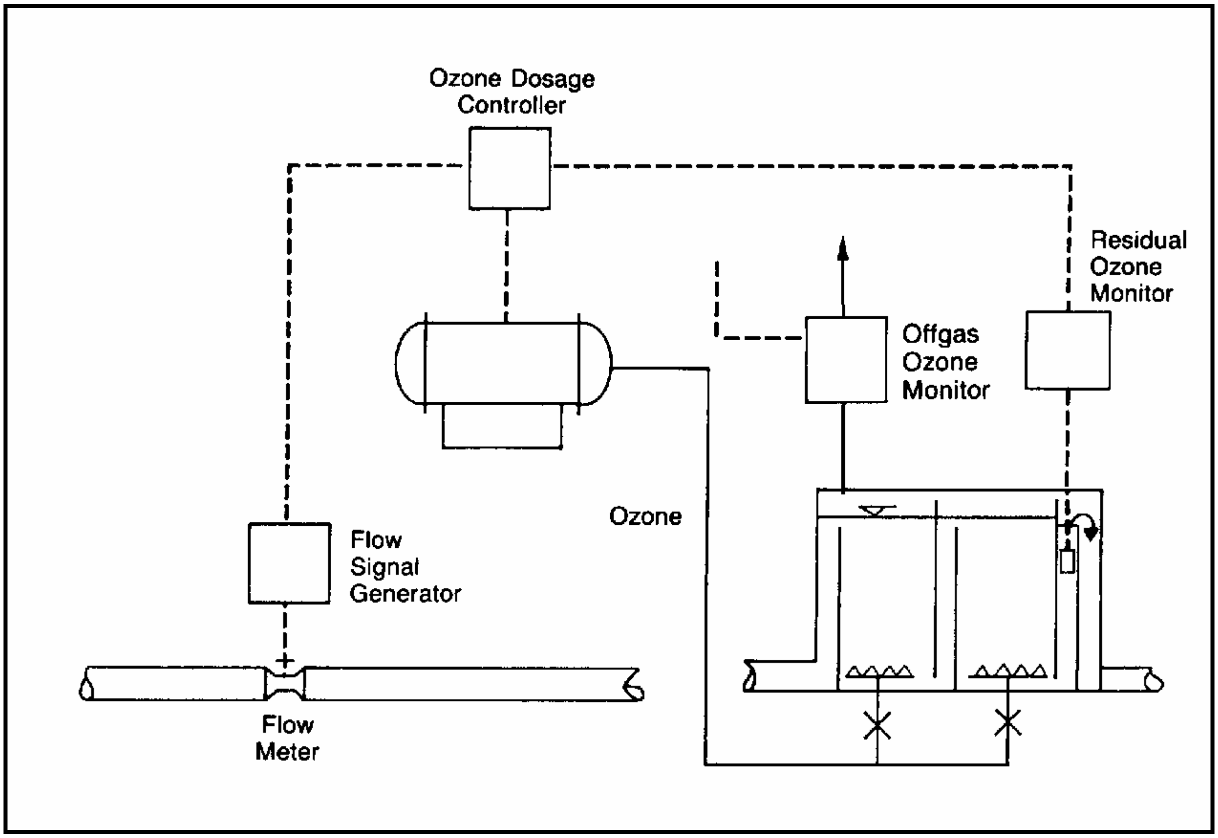

Figure 11. Ozonator Feedback Control Methods

1. Flow Pacing

If the treatment process requires a constant ozone dose, a 4-20 mA signal from a process flow meter can be used as an input signal to directly control the ozone output. This is straight proportional dosing and is the simplest form of control. Frequency controlled ozonators are more suitable for this type of control as the ozone output is linear to increasing frequency.

2. Ozone Residual

Most process waters have varying levels of contamination and therefore varying ozone demands. The use of devices for measuring residual ozone concentrations in the treated water may be used to determine whether the ozone demand has been met. These instruments usually provide a 4-20 mA signal to a PID controller that can then automate the ozone output from the generator. The limitation is that water flow rates must not vary greatly, unless a flow compensation circuit is included.

A combination of both flow pacing and residual measurement can be used in a cascade control where the flow or ozone residual is the primary influence and the other is used to bias the output control signal.

3. Off-gas Concentration

Similarly to measurement of an ozone residual, measurement of the ozone concentration in the off-gas may be effectively used to automate the ozonator. In a correctly designed diffusion and contacting system, a specific concentration of ozone remaining in the off-gas will indicate that the ozone demand has been met and a residual has been achieved.

With the current measurement and control technology, rather complex automatic systems can be implemented which can rationalise the amount of equipment needed and reduce the number of generator units required for specific treatment applications.

Such an example is where a single ozone generator is installed, however several processes are treated with individual automation systems. This requires the ozonator to act as a slave unit whereby a constant ozone concentration is maintained irrespective of the gas flow through the unit.

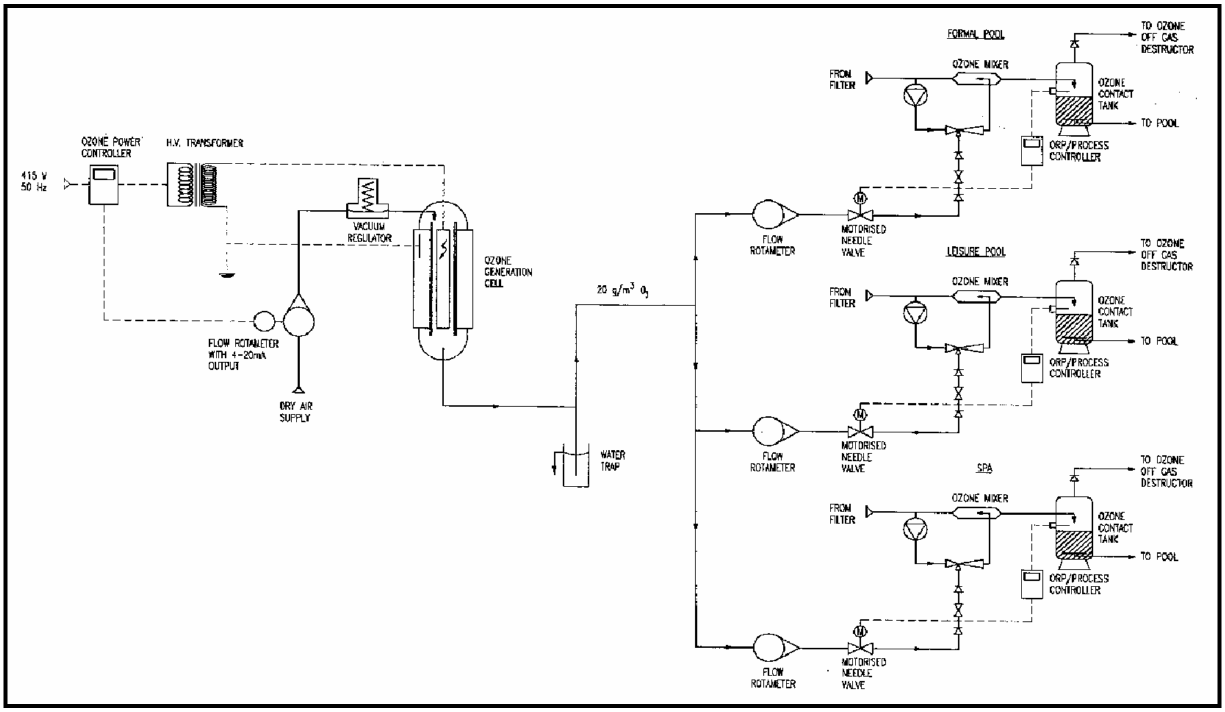

Figure 12. Automation Control by Constant Concentration

OZGEN OZONATION EQUIPMENT

Watertec Engineering Pty Ltd manufactures the ***Ozgen*** range of water cooled corona discharge ozone generators with output capabilities of 10 g/h to 3 kg/h.

Ozgen ozonators are of the vertical tube design using medium frequency generation technology and PLC control systems. These ozonators are manufactured in Australia to the highest quality standard, ISO9001, and are exported to many countries throughout the word. *Ozgen* ozonators have been in continuous field operation since 1992 and have established a reputation of being a quality, reliable and cost competitive product.

The *Ozgen* range was developed with careful consideration of the operational problems experienced with most ozone generators of equivalent outputs, available worldwide. In doing so, many special features have been incorporated which are reflected in the equipment's proven performance and reliability.

Ionics Watertec also manufactures a comprehensive range of ancillary equipment necessary to provide a complete ozone facility, including; injectors, diffusers, off-gas destructors, gas venting valves and automation packages.

Following is a summary of the main features of the *Ozgen* ozonator range.

THE *OZGEN* OZONATOR

- **Australian made:** *Ozgen* ozonation equipment is designed and manufactured in Brisbane, Australia by Watertec Engineering Pty. Ltd.

- **Computer control:** Modern PLC control and power electronics have been used for the overall operation and ozone generation process.

- **Medium frequency:** All *Ozgen* ozonators operate at medium frequency using state-of-the-art IGBT inverter technology.

- **Flexible control:** The frequency controllers have been specifically designed to provide a high degree of flexibility for optimisation of the ozone generating process.

- **Balanced load:** Due to the frequency control system used, the 3-phase supply is full balanced.

- **Moderate high voltage:** With the medium frequency generation technology, the high voltage used in only 8.5kV which greatly reduces dielectric stress and minimises maintenance requirements.

- **Matched transformers:** To eliminate harmonics, the HV Transformers are purpose wound and matched to the frequency control system.

- **Output meter:** An ozone output meter which is calibrated in g/h O_3 is provided on all units.

- **High turndown:** All *Ozgen* ozonators may be regulated from 0-100% output, either manually or automatically via a 4-20 or 0-20mA control signal.

- **EPROM backup:** All of the operation and alarm functions of the E and AR series ozonators are controlled by a programmed logic controller with EPROM facilities.

- **RS232 facilities:** All *Ozgen* ozonators include RS232 facilities for connection to remote computer equipment.

- **Low power consumption:** *Ozgen* ozonators are very power efficient due to the medium frequency generation technology.

- **Mimic panel:** The 'AR' Series ozonators incorporate a diagrammatic mimic panel on which all function and alarms are individually enunciated.

- **Ozone concentration control:** All *Ozgen* ozonators may be operated with either a fixed flow variable concentration output or a fixed concentration, variable flow output. This has significant benefits where more than one ozone injection point is to be supplied from a single ozonator.

- **Air or oxygen feed:** *Ozgen* ozonators may be operated on dry air, pure oxygen or an air/oxygen mixture.

- **Common Air Supply:** With a separate pressure fed air preparation system, several ozonators may be supplied from a single air preparation plant.

- **Vacuum operation:** The *Ozgen* vacuum control valve enables a pressure fed air preparation system to be used in conjunction with vacuum ozone injectors. With this design all components and pipework which contain ozone operate under vacuum which is the safest possible way of operating an ozone facility.

- **Low cooling water flow:** Due to the efficient design of the ozone generation cell, the cooling water flow requirement is far lower than other ozonator types. Also, the ozonator output is not de-rated with an increase in cooling water temperature, up to 30°C.

- **Fully protected:** The alarm facilities provided monitor up to 19 ozonator functions. Therefore, *Ozgen* ozonators are protected for all conditions that are likely to cause problems or damage components.

- **Low maintenance Costs:** With the vertical tube generation cell design the initial capital and subsequent maintenance costs are far lower than other ozonator designs.

- **Operation during maintenance: The** ozone generation cells are provided in 100g/h modules, using air as the feed gas. Therefore, with ozonators above 100g/h the units may be operated with 1 or more cells disconnected or removed for maintenance.

- **Low cost cell:** Due to the low cost of the ozone generation cells, spare units may be kept on site to ensure that the ozonator remains at full capacity during routine maintenance.

- **Tailor made cabinets:** all *Ozgen* ozonators include powder coated steel cabinets.

- **High quality:** All *Ozgen* ozonators are manufactured to the highest international quality standards.

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