Electrolytic Ozone for Pharma Purified Water

By V. Baratharaj

"The choice of electrolytic ozone is determined by the end use of water."

The pharma industry perhaps requires the most purified water. Water treatment assumes a very important role in maintaining standards that are so very stringent. It has been noted that often use of ozone in pharma industry is in similar lines as ozone used in industrial water treatment. Using ozone in the pharma industry means consideration of various design factors to maximize ozone benefits. This article attempts to explain why ozone produced by electrolytic method can be the choice for pharma purified water. ☞ www.otsil.net

The properties of ozone are well known. However, some of its properties are most suited for the pharma industry. But, what are these properties so-sort-after by the pharma industry?

Lets us list some important aspects considered by the industry:

- You need a very powerful oxidizing agent that will be effective against most pathogenic species .That is to say like an broad spectrum antibiotic, the oxidizing agent must be a broad spectrum agent, effective against bacteria, virus strains, unicelluar organisms and at the same time oxidize unwanted organic compounds in the water.
- You need an oxidizing agent that acts quickly and efficiently in very small concentrations.
- You need an oxidizing agent that is very effective at pH 7 and at say 25 degrees water temperature.
- You need an oxidizing agent that is either rapidly consumed or decomposes without

Ozone Concentration ppb	Pc. Claviforme	Staph Aureus	Micrococcus Luteus	B. Subtilis	Serratia species	Ps. aeruginosa
25-50	60	60	120	180	180	180
approx. 100	40	40	90	120	120	120
approx. 200	20	20	40	50	60	90
1000-2000	10	10	10	20	15	20
4800-5000	1	1	1	1	1	1

Table 1: Destruction Time in Minutes - Initial Bacterial Count 1000/ml

leaving any residue. It has to have a very short span of life in ultra pure waters.

Ozone supercedes any other technology in consideration of the above requirements of an ideal oxidizing agent for the pharma industry. Some of the microbial properties of ozone are listed in Table 1 (The most problematic pathogenic species have been considered here). At 4800-5000 ppb concentration, ozone destroys the most resistant strains of pathogens within one minute of exposure. The ozone, therefore, becomes the most sorted after disinfectant.

How is Ozone Produced - Why Electrolytically Generated Ozone?

Ozone is formed by the reaction of highly reactive atomic oxygen with the stable oxygen molecule O_2. This reaction of formation is always limited by the competing reaction. The same species that produces ozone, is responsible for its destruction.

There are various ways of producing atomic O:

- From oxygen by energetic photons (ë < 185 nm, "hard" UV radiation):
- From oxygen by high voltages in a plasma (discharge)
- From water by electrolysis at the surface of the anode

Ozone production relies on either of these primary processes:

- Ozone production by UV radiation
- Ozone production by electrical corona discharge
- Electrolytic ozone production

Production of Ozone by UV Radiation

This type of ozone production is responsible for maintaining the ozone layer in the earth's stratosphere. For technical applications the efficiency of the process is usually too small to be economic, except for the production of small ozone quantities with usually small ozone concentrations. However, UV radiation is not an alternative for applications where water is required in larger quantities - the UV stations would be too large and the energy costs too high. If ozone is required in larger concentrations and quantities, only the other two methods of producing ozone remain.

Production of Ozone by Electrical Corona Discharge

The method of ozone production using electrical corona discharge involves equipment in which ozone is produced from pure oxygen and the oxygen in the air (gaseous mixtures) with the assistance of a high-voltage. This type of ozone production is currently the most economic process for larger scale applications. The disadvantage of its use in ultrapure water systems is that it is a high voltage device and that it requires an operating gas of very high purity, which is expensive and which ultimately means a disturbing "gas bubbles" in the water.

Production of Ozone by Electrolysis

This process does not exhibit the above-mentioned disadvantages for applications in ultrapure water systems. The electrolytic cells used for ozone production are typically fed with DC voltages of a few volts from a special power supply unit. Electrolytic ozone generation requires pure water as feed. This means that ozone is produced in situ using the water to be treated as feed. The water needs to be purified, with a conductivity of <20 µS/cm, which makes electrolytic ozone generation the ideal technology for ultrapure water applications.

Advantages over Electric Corona

Ozone by electrolysis for purified water provides the following benefits:

- No formation of Nitric Oxides (NOx) which in turn react with moisture to form Nitrous Acid (HNO_2)
- No high-voltage device required
- Ozone generation is directly from the water where it is used immediately
- More efficient ozone mass transfer
- High ozone concentration in the water possible
- No feed gas preparation
- No gas ballast in the water
- No substances emitted through high-voltage discharge introduced into the water via the gas
- No expensive injector systems with valves to protect the high-voltage device

Ozone generation on the principle of electric corona discharge is mainly used in industrial drinking/process water applications where it is economical. However, this older process has no longer been customary for the past two decades for the storage and distribution of process water qualities in the pure and ultrapure water applications and in particular of pharmaceutical water and qualities similar to pharmaceutical water. The very high ozone concentrations often requested in the past are not necessary in ultrapure water storage and distribution systems, and are even counterproductive sometimes. This is also reflected in the "Baseline Pharmaceutical Engineering Guide".

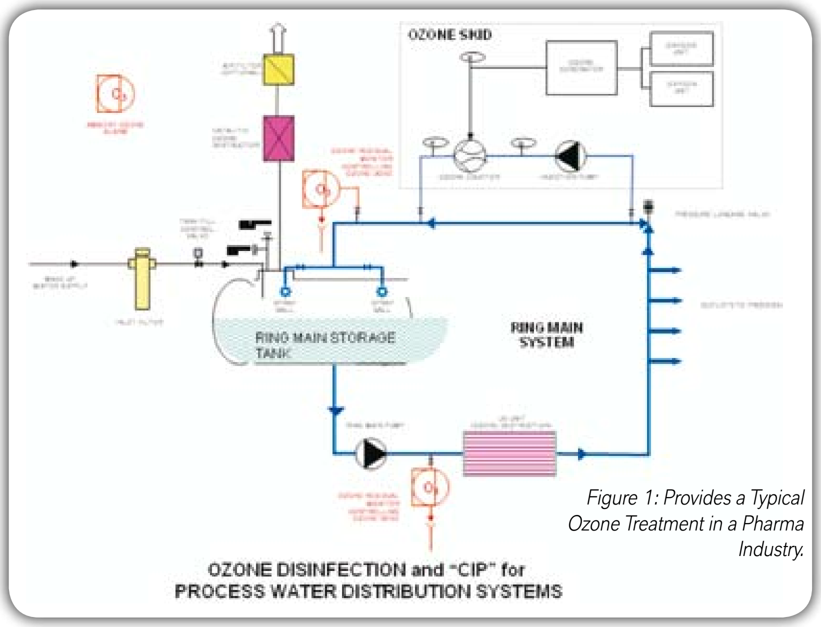

Figure 1: Provides a Typical Ozone Treatment in a Pharma Industry.

Electrolytic Ozone Production

Electrolytic ozone production relies on a simple process, the electrolysis of water. If a dc voltage exceeding the decomposition voltage of water is applied to an electrolysis cell, an electrical current flows and gas bubbles evolve from the electrode surfaces. On the anode (+) they consist of oxygen and on the cathode (-) of hydrogen. The electrical current decomposes water in its elements. The quantity of the formed gases is directly proportional to the electrical charge flowing through the cell (Faraday's law), the rate of gas evolution is proportional to the electric current. The decomposition voltage, or minimum potential needed for the process corresponds to the chemical energy which is stored in the oxygen and hydrogen. The electrochemical reactions of water splitting and gas formation take place at the surfaces of the electrodes.

Ozone is only formed at the anode if it is coated by a specific electro catalyst. The energy and therefore the chemical reactivity of the adsorbed oxygen, formed as an intermediate of oxygen evolution, increases with increasing voltage. If the cell voltage exceeds approx. 2.3V, the energy of the adsorbed oxygen corresponds to the one of free oxygen. Free oxygen can react with molecular oxygen to ozone. Because of the low temperature in the electrolysis cell and the absence of reactions leading to ozone destruction, the ozone concentration which can be reached is higher than in ozone generators based on silent electrical discharge.

For the electrolysis of water, a solid electrolyte is used in place of the necessary liquid electrolyte. The solid electrolyte consists of a functional, chemically resistant polymer with the capability to transport cations/protons. At the same time, the membrane is used as a physical separator for the products of the electrolysis. The ozone yield is proportional to the applied cell current. The electrode material must be resistant to chemical and electrochemical corrosion. The electrodes must be manufactured to high precision to guarantee good contact with the membrane and an even current distribution. Porosity must be sufficiently open to avoid accumulation of trace impurities within the pores.

Chemical/Physical Laws and Correlations for the Dissolution of Ozone in Water

Ozone is a gas which dissolves in water to a certain extent (approx. 13 times more than oxygen). Ozone is increasingly unstable in a dissolved state (forced metastability). A number of parameters influence this stability.

Temperature: An increase in temperature has a negative effect on the stability of the ozone molecule Disintegration is accelerated. The higher the temperature, the lower its solubility in water.

pH value: Ozone reacts with hydroxide ions (OH-): In this case the higher the number of ions (high pH value), the faster the ozone will disintegrate. Conversely, the decomposition is slower with a lower pH value. When ozone decomposes in water the hydroxyl radical (OH) is produced. The reaction between hydroxide ions (OH-) and ozone lasts until the ozone has completely decomposed.

Contact with catalytic materials or with short-wave light: UV radiation with a wavelength of 254 nm leads to an accelerated ozone disintegration.

Oxidizable Substances: The presence of oxidizable substances always consumes ozone.

Process and Design Aspects

Having produced ozone, the basic question is to transfer this ozone into the water and ensure that the ozone remains in the water. Since ozone is produced in high concentrations in the water itself, the transfer aspects are addressed very well. Ozone is not known to dissolve in war very well. It is not stable for long periods. A premature escape of ozone as a gas has to be avoided .Observations have shown that ozone in pharmaceutical water plants has a half-life of approximately 20-30 minutes .Since these observations have been made in different plants, the above parameters have to be viewed with caution as reference data in general.

In principle, a shorter sanitisation interval is viewed to be better because safer. For sanitisation, a smaller ozone concentration with a longer duration is viewed to be more favourable. If ozone concentrations greater than 50 ppb are used for a sanitization process, (for the reasons mentioned previously) the ozone concentrations must be reduced through natural decomposition (natural half-life period, without forced ozonolysis through UV-radiation) to less than 50 ppb (below 50 ppb the forced ozonolysis through UV-radiation can take place).

How can Ozone decomposition be accelerated in pharmaceutical water?

Ozone decomposition has to be accelerated in pharma water before use. In addition to the "natural" ozone disintegration (according to the half-life curve), it is also possible to greatly accelerate this process using UV light. Using UV systems with maximum radiation at: a wave length of: 254 nm and radiation intensity of >600 J/m^2.

The ozone concentration in the pharmaceutical water distribution system is reduced to a measurable <5 ppb. The output of UV at 254 nm hydrolyzes ozone with water to produce free hydroxyl radicals (OH). This reaction is significant at pH above 6 or with a very low UV intensity. With a lower pH value or a higher UV intensity the ozone disintegrates to H_2O_2 before this has a chance to react with the residual ozone to produce OH radical. This process is not desirable for the pharmaceutical water application. The rule is therefore only as much ozone as suitable for the microbiocidal purpose and only as much UV radiation intensity as necessary to destroy the ozone.

Residual Ozone Distruction in the Storage Tank

This is mostly by using catalytic ozone distructors .The energy introduced for ozone generation is released again during catalytic ozone destruction. This is, therefore, an exothermal catalytic reaction. Ozone gas enters the ozone destructor and decompose here, releasing heat to produce oxygen and leaves the device in this form. The catalyst consists of a specially activated noble metal mixture on a metal oxide substrate. The housing material is normally titanium passivated stainless steel.

Water Qualities Have Improved - Lesser Ozone Required

Generally speaking, the quality demands placed on pharmaceutical water has risen steadily over the past 20 years. One reason for this development is the increasing globalisation of pharmaceutical production. The fact that production is not only geared to one local market has meant that strictest limit values must be observed if the products are to be authorised globally. In the mid nineties the above mentioned requirements for low TOC, conductivity and endotoxins etc. meant that electro-deionisation (EDI) became an increasingly popular non-thermal method of treating pharmaceutical water. With the assistance of this technology, conductivities of < 0.1 µS/cm (approx. 8% of the requisite limit value) and a TOC value of < 5 ppb C (approx. 1% of the requisite limit value) have become feasible. The plant design for storage and distribution systems, the types of fittings used and the surfaces coming into contact with media in terms of materials and surface properties, as well as the nature of the welded seams, have also undergone further development. This means that less ozone is consumed in the systems and that consequently a smaller amount of ozone is required.

Ozone UV Combination Benefits

On the one hand ozone acts as a cell toxin and due to its high oxidizing strength destroys the cell wall and membrane; the cell loses its cytoplasma and can not reactivate; the microorganisms die off. On the other hand UV radiation similarly damages the cells. Thus, for example, hard UVC radiation with a dosage of approx. 400 J/m^2 is used for the treatment of drinking water. Apart from the individual germ-reducing properties, the combined use of ozone and UV additionally provides the possibility to remove TOC by oxidation. The ozone is split photochemically and reacts with water to produce OH (hydroxyl radical). OH takes a hydrogen atom from an organic molecule (R-H) and forms an organic radical (R). This can react with oxygen, for example, to produce a peroxyl radical which reacts further in different reactions to produce more stable intermediate products ultimately through to complete mineralization to produce CO_2).

In addition to the "natural" decomposition of ozone (in accordance with a plant-specific half-life curve) it is also possible to greatly accelerate ozone decomposition with UV light. As a result, a part of the distribution system can be kept "under ozone" (usually the storage tank) whilst a different part (e.g. the distribution loop or the consumer - point of use) is "kept free from ozone" by activating a UV station. Using UV systems with maximum radiation at a wave length of: 254 nm and radiation intensity* (dosage) of: >600 J/m² the ozone concentration in the pharmaceutical water distribution system is reduced to values below the detection limit.

Does it mean that we cannot Use ozone generated by Corona in Pharma Purified water?

The choice of electrolytic ozone is determined by the end use of water. For example water used for production of insulin should ideally be produced by electrolysis method. Water used for compounding, such as oral liquids etc can be treated with corona ozone. Water required for CIP process in pharma Industry can be ozoned by the conventional corona method. However, care is to be taken on the design of ozone mass transfer, residual ozone removal and finally vent ozone distruction. Ozone by corona method still finds an important place in pharma purified water.

About the Author

Mr V. Baratharaj is the CMD of Ozone Technologies and Systems India Pvt Ltd, a Chennai based company specialising in ozone applications. He has more than 20 years' experience in ozone technology and is the founder secretary of the Ozone Association of India. Ozone Technologies & Systems (India) Pvt. Ltd. more popularly known as OTSIL was formed in May 1994. Over the last 15 years OTSIL had been promoting the use of ozone, the most eco-friendly product the World has ever known. OTSIL has been innovative enough to make ozone applications more economical and user friendly. ITT-WEDECO Germany, the world's largest ozone company, has vested with OTSIL the sole responsibility to represent them in India.

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