

OZOMAX LTD

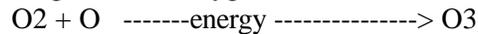
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Ozone Oxidation Capabilities

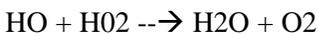
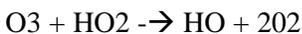
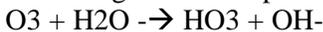
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Introduction

Discovered in the 19 Th. century Ozone a natural form of activated oxygen (allotropy) generally produced during lightning storms and continuously occurring in the stratosphere due to action of ultraviolet (UV) is being rediscovered for the 21 Th. century. It can be artificially produced by the action of high voltage discharge in air or oxygen.



Ozone is highly unstable and must be generated on site. Its oxidation potential (-2.07V) is greater than that of hypochlorite acid (-1.49V) or chlorine (-1.36V), The latter agents being widely used in water treatment practice. Ozone is thought to decompose accordingly (Miller 1978, 167-168):



This unstable form of oxygen breaks down to oxygen molecules and oxygen atoms which have high oxidation potential. If we examine the oxidation power of Ozone by measuring the REDOX potential will find out that O₃ is about 5 times more oxidising than oxygen & about twice as much as Chlorine. These high potentials increase its reactivity with other elements and compounds. This reactivity is about 20 to 50 times more reactive than chlorine and Permanganates as it is well documented in the case of the high kill rate of micro-organisms (Funguses, Bacteria & Viruses). This high kill rate means smaller retention times, storage tanks, are required to do the same disinfecting as other oxidants. In other words the capital cost for building these tanks and treatment plants are reduced considerably.

Ozone is a God given gift as it will reduce chemical handling, storage, transportation infrastructure and production facilities. Ozone requires only electricity which is readily available from hydro, solar, wind or fuel electric generators. In many instances O₃ will allow decentralisation of services which will provide better flexibility and better cost management. Here is non exhaustive list of Ozone applications where data & references are available:

Ozone chemical free treatments and applications

<u>Waste water effluents</u>	<u>Industrial /Agriculture</u>	<u>Food Industry</u>	
<u>Others</u>			
Domestic/Municipal Pulp & paper	Cooling towers treatment Boiler water treatment	Drinking & water bottling Grain silo disinfecting	Smoke & odour treatment Semiconductor wafers clean
Mining (Cyanide, Arsenic) Pharmaceutical (Phenol)	Chilled water treatment Cutting fluids recycling	Fruit & vegetable storage Meat storage	Laundry water recycling Med. instrument sterilisation
Textile	Barn disinfecting (air/water)	Slaughter house disinfecting	Hospital air sterilisation
Leather Petroleum/Petrochemicals	Hydroponics Animal waste treatment	Fruits & vegetable wash Food containers sterilisation	Aqua-culture Paper pulp bleach
Electroplating	Water dripping treatment	Wine/Beer SO ₂ replacement	Sour gas desulfurisation
Heavy metal precipitation Landfill leachates	Animal drinking water Irrigation water disinfecting	Chicken egg wash Ozonated meat grinders	Zebra mussels treatment Rubber recycling,.....etc.

The question we should ask is if O₃ is so good why O₃ is not widely spread ? The answer is simple which is up to recent times Ozone generators (mid-range) were very expensive with an average of cost of \$ 7000 US/Lb/day with advent of new materials, power supplies, high frequency generators prices are starting to go down around \$ 4000 US/Lb/day with an outlook in the near future around \$ 2000/Lb/day or even lower at this level of prices Ozone will compete with the other oxidising alternatives such as Chlorine, Hydrogen peroxides,.....etc.

The time has come where this chemical free technology is an affordable reality.

Design consideration

This section examines the different design considerations which must be made when designing an ozone treatment system. The following topics are discussed:

- 1) Organic and inorganic load
- 2) Ozone dissolution
- 3) Ozone injection alternatives
- 4) Post ozonation requirements

*** Organic and Inorganic Load**

The reaction of ozone with most organic compounds may be modeled using a first order kinetic equation:

$$\ln (C/C_0) = -kt \quad (1)$$

where k is the reaction rate constant. The value of k is found by carrying out laboratory experiments. Typical values range from $4 \times 10^{-3} \text{ sec}^{-1}$ to $4 \times 10^{-4} \text{ sec}^{-1}$. The value of k measured under ambient conditions and neutral pH may be adjusted to account for the effects of pressure, temperature and pH as follows:

$$k'' = k'(b P/P_a)(c T/T_a)(d \text{pH}/7)$$

(2)

where the subscript (a) represents ambient conditions.

Although Eq.2 implies that the reaction rate increases with increasing temperature, as is generally the case, it must be kept in mind that ozone solubility is adversely affected by increasing temperature. The effect of pH is illustrated in Figure 1.

The effects of these variables are captured in OZOCAL, a software developed by Ozomax Ltd. OZOCAL estimates the ozone dosage required to treat a given effluent based on its analysis. Typically, for organic contaminants 0.1 to 1.6 g O₃/g COD is needed. The oxidation of heavy metals such as iron and manganese if present alone generally occurs in stoichiometric proportions.

*Ozone Dissolution (Mass Transfer)

For the diffusion of ozone from a gas bubble to an aqueous fluid the boundary conditions are such that the Fick's law simplifies to,

$$N_A = d_L * C \quad (6)$$

where C is the ozone concentration within the bubble and d_L is the mass-transfer coefficient as defined in Eq. 7,

$$d_L = 2D_{AB}/D_p + N \quad (7)$$

where D_p is the bubble diameter and N is a function of the Schmidt Number.

Equations 6 and 7 reveal two very important characteristics of ozone dissolution.

- 1) O₃ dissolution increases with the gaseous ozone concentration
- 2) O₃ dissolution increases with decreasing bubble diameter.

To take advantage of these two points the ozonator must be designed to efficiently dissipate heat which would otherwise cause the premature conversion of the ozone to oxygen thus lowering its concentration. Also, an oxygen feed may be used to yield higher ozone concentrations than those obtained from air. (See Figure 2) Secondly, the ozone/water contact should be made under pressure in order to produce small bubbles. (See Figure 3)

The maximum number of moles of O₃ transferred to the solution may be calculated from,

$$M_{O_3} = N_A * S * t \quad (8)$$

where S=total bubble surface area

t = contact time

This reveals a third important ozone dissolution characteristic:

- 3) O₃ dissolution increases with increasing retention time

Equation 8 also confirms point (2) above.

In summary when ozone is used to treat water or wastewater, it must be transferred from the gas phase, in which it is generated, to the liquid phase. Ozone is 12.5 times more soluble in water than oxygen.

The single most important variable that affects ozone mass transfer is the concentration of dissolved ozone- reactive materials in the water. Ozomax ozonators will produce O₃ concentrations from about 4 to 10 % with Oxygen feed however, the optimum concentrations for generating ozone are 5-6% wt with oxygen used as the feed gases.

* Ozone Injection

The principle methods currently used to introduce ozone into water and wastewater are:

- 1) contact column
- 2) venture injection
- 3) centrifugal injection

*Post-Ozonation Requirements

The ozonation treatment step is usually followed by :

1)Clarification: to precipitate oxidized organic and inorganic matter

2)Filtration

(nano, sand, charcoal): to remove precipitants. The use of activated carbon filters has the added advantage of adsorbing the excess unreacted, unrecycled ozone and allows it to convert back to oxygen.

3)O₃ destruct in air vents: may be accomplished using thermal, catalytic or ultraviolet destruction

Oxidation Mechanism

The free radicals (HO₂ and HO) react with a variety of impurities such as metal salts, organic matter including micro organisms, hydrogen and hydroxide ions. They are more potent germicides than hypochlorite acid by factors of 10 to 100 fold and disinfect 3125 times faster than chlorine (Nobel 1980).

Oxidation potential does not indicate the relative speed of oxidation nor how complete the oxidation reactions will be. Complete oxidation converts a specific organic compound to carbon dioxide and water. Oxidation reactions that take place during water treatment are rarely complete, due to the large quantity of contaminants and relatively short durations of time in which to oxidize the water pollutants.

Therefore, partially oxidized organic compounds, such as aldehydes, Carboxylic organic acids are produced during the relatively short reaction periods.

These aldehydes and carboxylic acids can be removed by other means prior to complete mineralisation to reduce the amount of Ozone needed for complete oxidation of these chemicals.

There are three fundamental mechanisms which apply to the oxidation of organic compounds reacting with an oxidizer. Each mechanism is unique as to how organic compounds react with an oxidizer. But, in some cases, oxidants will react with organic compounds by all three mechanisms, although in sequential steps.

First. The addition mechanism which occurs with organic compounds containing aliphatic unsaturates, such as olefin. Ozone can add across a double bond to form an ozonide. This reaction occurs readily in nonaqueous solvents, but as soon as water is added, the ozone hydrolyzes to other products, with cleavage of the former double bond .

Second. The substitution mechanism involves replacement of one atom or functional group with another.

This specific reaction also can be viewed as an insertion reaction, whereby oxygen is inserted between the ring carbon and hydrogen to form the hydrogen group on the ring .

Oxidation also can involve cleavage of carbon-carbon bonds to produce fragmented organic compounds.

Effect of Temperature and PH

It is clear that other parameters affect the reaction mechanism and rates as found by various studies. The effectiveness of ozone to oxidise organic and inorganic compounds is function of to the temperature of the water and pH levels. In wastewater applications there are many variables such as: water temperature, pH, COD, BOD, TSS, heavy metals, which need to be considered.

Ozone, at low pH levels (less than 7), reacts primarily as the O₃ molecule by selective and sometimes relatively slow reactions. Ozone at elevated pH (above 8) rapidly decomposes into hydroxyl free radicals, which react very quickly. Many compounds that are slow to oxidize will oxidize rapidly when the pH is adjusted to the Alkaline side. It was found that PH=8-10 is most suitable for organic molecules oxidation.

The initial step of the decomposition of ozone is the reaction between ozone and hydroxide ion to form ozone ion and hydroxyl radical (OH⁻): The hydroxyl radical then reacts further. This process would explain the increased dissociation of ozone with increasing alkalinity. Recently, studies have shown experimentally that as pH increases, the kinetics of ozonation of organic compounds changes. Hydroxyl radicals may be the important active species in ozonation as has been concluded (Glaze 1980).

Therefore, the alkalinity of the water is a key parameter in advanced oxidation processes. Ozone then decomposes rapidly in water with a half life of a few minutes about 20 minutes in room temperature but could be much faster less than 10 minutes in the presence of bicarbonate and carbonate ions which are excellent scavengers for free radicals.

In addition, carbonate ions are 20 to 30 times more effective in scavenging for hydroxyl free radicals than bicarbonate ions. For that reason we stated that the pH of 8.0 to 10.0 is most appropriate for ozonation as it was found that at that PH > 10 the bicarbonate ions convert to carbonate ions (EPA 1989).

Effect of catalysts :

There are several catalysts used in conjunction with Ozone such as semi-precious and precious metals, ultrasonic agitation, H₂O₂, electro-coagulation but the most commonly utilised and well documented are the ultraviolet rays at wave length of 254 nm..

Ultra-Violet has been found in the past 10 to 15 years that when this treatment is combined with Ozone there is a rather «explosive» reaction as the two in a sense «destroy» each other creating a highly reactive Hydroxyl ion. The end results of this is that many compounds that neither UV or Ozone independently can remove, however with the combination of these compounds can be removed and the rate of removal is extremely rapid. Sometimes in as little as two seconds. The produced free radicals of this reaction contain at least four radicals: (O) Excited Atomic Oxygen species, (HO) Hydroxy radicals, (H₂O[•]) Hydroperoxy radicals and Excited Carbon containing species.

Compounds normally refractory or slow reacting to Ozone or UV alone but which react to the combination of such organo metallic complexes, Cyanides, Phosphorous and nitrogen compounds

Ultrasounds has not been fully exploited as applied to waste water treatment nor fully understood nor documented at present. It is known that in many cases it works with the Ozonation treatment in ways quite similar to UV. Principally it excites the ionic structure of both the water and the contaminants in the waste stream and as a result the Ozonation process is expedited (either in speed of reaction or it actually causes a reaction where the contaminant had been refractory to the Ozone treatment).

ELECTRO-COAGULATION is the process of applying a direct or alternating electrical current and voltage of varying strength to electrodes contacting water or waste water which results in the formation of Floc which can be filtered to remove suspended and flocculated substances. The mechanism by which this flocculating occurs are complicated and involve the inter conversion of electrical and chemical energies reacting with and on substances in the water or waste water.

Waste waters which are slightly reactive to Ozone show excellent reaction with the Electrochemical method such as for domestic and textile waste waters. Ozomax own a patent pending Ozone electrolytic reactor which exploits the advantages of combining ozone and electrolytic processes.

Precious and semi precious metals catalysts studies by Ozomax Ltd were made at McGill University in Montreal showed that the presence of such metals speed up the reaction rates which in some cases can double or triple. 100 % mineralisation occurs when combining these types of catalysts with Ultra violet at 254 nm.

Conclusion

This quick synopsis about ozone usage and applications shows that it is simple and easy to use once it is understood. All variables such PH, temperatures, pressures and catalysts were captured in a software developed by Ozomax Ltd which can predict the ozone quantities required to treat a certain flow rate of a given chemical analysis.

But it is now obvious that Ozonation should now be considered in treating difficult waste waters (heavy metals, textile effluent, plating,.. without or minimal use of other chemicals.