# OZONE GENERATION

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## Contents



## Summary

An overview on ozone generation history, ozone physical and chemical properties is presented. The main types of ozone generators (electrical discharge and electrolytic cell) have been described in more detail by capacity, ozone concentration and energy consumption. The conventional water ozonation flow sheet has been presented and process control options characterized. Aspects of ozone safety have been discussed.

## 1. Introduction

### 1.1. History and Application

Ozone (trioxygen) was quite accidently discovered in 1785 by van Marum, the Dutch chemist who led electric current through oxygen. The name “ozone” (*ozo* = “smelling” in Greek) was given to the unknown gas by the German chemist Christian Schöenbein in 1840, who is now called the ″godfather of ozone″. By 1867 the identity and structure of ozone was confirmed with scientists looking towards its usefulness.

Ozone started to be used for disinfection of drinking water in Europe already at the end of the 19th century. The first ozonation plants were put into operation in Germany (Wiesbaden and Paderborn) in 1896, in Paris (Saint-Maur) in 1897/1898, and in Holland (Oudshorn) in 1898. On the 1st of January 1911 was in Petersburg (Russia) put into operation the biggest ozonation plant in the world this time (50 000 $m^3$/d of water).

It was in successful operation till the Civil War (1919). Since 1960 several thousands of European water treatment plants have applied ozone for surface water pre-or intermediate treatment.

In the USA ozone was first used in 1908, with minimal growth until 1985, mostly for wastewater disinfection purposes. Later ozone found its way also to the drinking water treatment processes. Within the past 25 years more than 400 ozone treatment plants have been designed, constructed, and operated to address drinking water disinfection, DBPs, taste and odor, color, microcoagulation, hydrogen sulfide and other needs (Rakness, 2005).

### 1.2. Physical and Chemical Properties

Under normal pressure and temperature ozone is a bluish gas with the characteristic intensive odor, about twice heavier than air. It's boiling-point is (-111,9 °C) and melting-point (-192.5 °C) at 0.1 MPa. Pure (100%) ozone is at (-111,9 °C) dark-blue liquid, extremely sensitive to the smallest organic impurities, shaking, temperature/pressure changes and *very explosive*.

Common oxidants in water treatment have been chlorine, hypochlorous acid and potassium permanganate. Ozonation is one of the most efficient, relatively new chemical oxidation methods (Table 1).

| **Oxidation species** | **Oxidation power*** |
|---|---|
| Chlorine | 1.0 |
| Hypochlorous acid | 1.10 |
| Permanganate | 1.24 |
| Hydrogen peroxide | 1.31 |
| Ozone | 1.52 |
| Atomic oxygen | 1.78 |
| Hydroxyl radical | 2.05** |

* Based on chlorine as reference point (=1.00)

** Powerful oxidative species with extremely short life-time

Table 1. Relative oxidation power of some oxidizing species

Ozone is a very strong oxidant, its normal oxidation potential at 25° C is 2.07 V in acidic solutions and 1.24 V in basic solutions. Only fluorine and °OH-radicals have higher oxidation potential.

In ozone reactions with inorganic or organic compounds in water usually one from three oxygen atoms is active, the residual two are separated as oxygen molecule:

$$CN^- + O_3 \rightarrow CNO^- + O_2 \quad (1)$$

$$RCH_2OH + 2O_3 \rightarrow RCOOH + 2O_2 + H_2O \quad (2)$$

Dissolved ozone decomposes in water solutions the quicker the higher the pH. As a result several radicals (among of them the very active °OH-radicals) are formed:
The main steps of the °OH-radicals formation are:

$$O_3 + OH^- \rightarrow {}^\circ O_2^- + {}^\circ HO_2 \qquad (3)$$

$$O_3 + {}^\circ HO_2 \rightarrow 2O_2 + {}^\circ OH \qquad (4)$$

## 2. Ozone Generation Theory and Conventional Process Schematic

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 (v/v) in the stratosphere, thus the term - the ozone layer. Natural production of ozone is by either UV radiation or lightning.

As a commercially demanded treatment, there have been decades of research and development put into methods of ozone industrial production. Today there are four recognized methods (Smith, 2002).

- Corona Discharge
- Ultraviolet Radiation
- Electrolysis
- Radiochemical source

Electrical discharge, often also called silent discharge, ozone generators ionize molecular oxygen by applying high power alternating current to the gas (Gottschalk et al., 2002). Ozone is formed by recombination of ionized oxygen atoms and unionized molecular oxygen, as illustrated in Figure 1 (Rakness, 2005, p. 3).

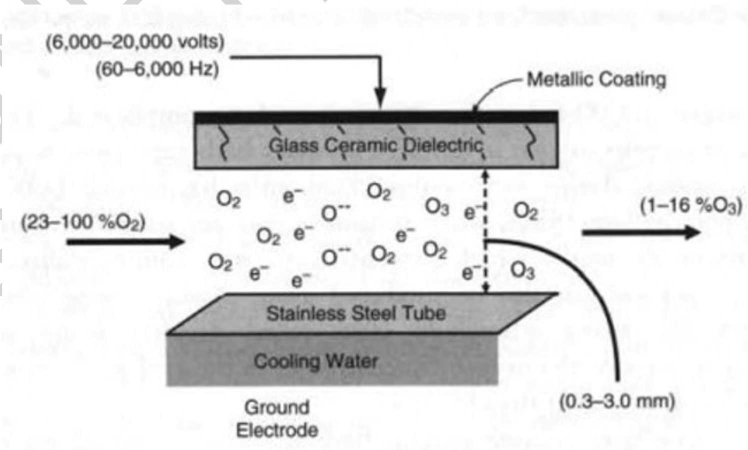


Figure 1. Principle of commercially available corona discharge ozone generator

Ozone synthesis reaction from the air or pure oxygen can be summarized as:

$$3O_2 \rightleftarrows 2O_3 + 298\ \text{kJ} \qquad (5)$$

This reaction is *reversible* - part of the produced ozone decomposes back to oxygen eliberating 149 kJ of energy per mole of ozone decomposed. The amount of liberated energy makes ozone in high concentrations dangerous. In this process only 4-12% of the energy supplied is used for the formation of ozone, the rest is transformed into heat.
An efficient cooling system has to be installed, because ozone decays fast at elevated temperatures, with $T_G$ = 50°C regarded as the critical value. In full-scale systems the gas is cooled to $T_G$ = 5-10°C.

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**Biographical Sketch**

**Rein Munter** was born in Tallinn, Estonia in December 23, 1936. He graduated from the Tallinn University of Technology in 1960 as a chemical engineer. Since 1960 his interests were focused on ozone impact on the Lake Ülemiste water parameters. He obtained his Ph.D in 1968 from the Tallinn University of Technology. In 1991 he defended the D.Sc degree in water chemistry and technology at the Kiev Institute of Colloidal and Water Chemistry (Ukraine). The areas of his scientific activities include ozonation and advanced oxidation technologies, groundwater treatment, green chemistry and technology, sustainable development. He has published more than 150 papers.