RESEARCHES ON WATER TREATMENT WITH OZONE

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Abstract. The first part of the paper presents the formation, the properties and the production of ozone; the factors that influence the generation of ozone (O_3) are highlighted. Later, to argue the introduction of a compressor in the operation scheme of O_3 generating, the pressure loss calculations are presented on a microbubbles generator (MBG). Two operation schemes to obtain air + ozone are exposed:

A) Installation scheme to produce ozone from atmospheric air;

B) Installation scheme to produce ozone from air with low nitrogen content.

The end of the paper presents the use of ozone in different areas and an implementation scheme of the ozone generator in an installation to for water treatment extracted from underground.

Keywords: ozone, ozone generator, water oxygenation.

1. INTRODUCTION

The ozone has the molecule consists of three oxygen atoms (O_3); normal oxygen molecule is composed of two atoms of oxygen (O_2). At ozone, the third oxygen atom can detach and can be combined with other agents [1] [2].

There is a distinction between ozone in high layers of the atmosphere, so-called stratospheric ozone and the ozone present in spaces in which we move and breathe. While stratospheric ozone is important and beneficial to human life because it shields the solar cosmic rays and harmful, preventing them to reach ground level, the ozone in the air we breathe, presents significant risks.

As a result of its high reactivity, ozone in high concentrations interacts with organic matter altering their structure. The ozone inspired into the lungs can lead to great damage. Even in relatively small amounts can trigger chest pain, coughing, shortness of breath and respiratory irritation. Also, the ozone can aggravate chronic respiratory diseases such as asthma and undermine the body's ability to fight respiratory infections.

According to Administration of Food and Drug Administration (AFD), medical devices used in enclosed spaces are not allowed to release, in the microclimate, a higher concentration than 0.05 ppm. Occupational Safety and Health Administration (OSHA) requires US employers to provide working conditions so that staff are not exposed to ozone concentrations greater than 0.10 ppm for 8 hours. Likewise, the National Institute for Occupational Safety and Health (NIOSH) recommends that the US limit of 0.10 ppm ozone is not exceeded ever, even for a short time. There are studies showing that ozone generating equipment's can increase the concentration of ozone above the safe established limits, even if used according to instructions. The concentration of ozone is influenced by several factors such as: the amount of ozone generated by the device, the size of the room where the appliance is placed, the volume of chemicals which the ozone can interact and the ozone concentration in the ambient air and the existing ventilation.

Experiments with so-called ionizers (different devices for ozone generation) showed that their effectiveness in removing particles such as dust, cigarette smoke, fungal spores, etc., is lower than air filters or electrostatic devices.

The ozone is a more powerful oxidant than chlorine on bio persistence organic substances present as pollutants in wastewater.

2. THE FORMATION, PROPERTIES AND OZONE PRODUCTION

The ozone is a gas whose presence is revealed by a slight pungent odor. The ozone is a gas molecule consists of three oxygen atoms. Free oxygen atoms (atomic oxygen O) act on molecular oxygen O_2 turning it into ozone (O_3) [3]:

$$2\cdot O + O_2 \rightarrow 2\cdot O_3 \quad (1)$$

Global ozone formation equation is:

$$3\cdot O_2 + h\upsilon \rightarrow 2\cdot O_3 \quad (2)$$

where hυ - is quanta of energy; υ- light frequency; h- Planck's constant.

The ozone formation from oxygen occurs with energy consumption:

$$3\cdot O_2 + 288,42\,KJ \rightarrow 2\cdot O_3 \quad (3)$$

When the reverse transformation occurs, the ozone releases the same amount of energy that was spent on the formation from the oxygen.

The light energy and electrical discharges can produce the reverse transformation:

$$2 \cdot O_3 \Leftrightarrow 3 \cdot O_2 \quad (4)$$

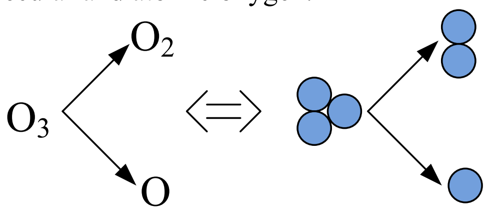
Because the ozone decomposes and turns into oxygen again according to previous reversible reaction, there can be a preparation of pure ozone, but only after oxygen ozonation.

The physical properties of ozone are [4] [5]:

- Molecular mass 48 kg / mole;
- Color: Blue;
- Smell: Pungent (garlic);
- Density: 2.144 g / dm^3 = 2.144 kg / m^3;

The ozone has a boiling point at -112.5 °C and a melting point at -1945 °C. The ozone is sparingly soluble in water, but more soluble than the oxygen.

The ozone is a gas stable only at low temperatures. Under normal conditions of pressure and temperature, the ozone decomposes into molecular and atomic oxygen.



The rate of self-decomposition of the ozone increases with temperature is water pH dependent, the nature and the concentration of dissolved salts. Its main property is the large chemical oxidation capacity.

The atomic oxygen released is very active which explains the strong oxidizing action of this gas; the molecular oxygen has a lower oxidizing action than the atomic oxygen.

The ozone is a highly soluble gas. At 25 °C the solubility of ozone is 109 mg/dm^3, and the oxygen solubility of 8 mg/dm^3. As a result, the ozone is 13 times more soluble in water than the oxygen.

It cannot obtain high ozone concentrations in water since it is highly reactive and reacts immediately with it, or with dissolved substances in water; normally, to achieve a concentration of 1 to 3% the ozone cannot be stored or transported but it can be generated.

This requires equipment's called ozone generators.

A classification of the ozone generators can be carried out as follows:

A) In terms of purpose, i.e. utilization:

- Ozone generators used in clinics, hospitals, nursing homes, kindergartens, schools, universities, hotels, restaurants, locations where the concentration of ozone should be less than 0.1 ppm;
- Ozone generators used in food warehouses, where there is no human person. Here, the ozone concentrations exceed 0.1 ppm.

B) In terms of the environment nature in which the product ozone is introduced:

- Ozone generators that introduces the produced ozone in another gas or gases;
- Ozone generators that introduces the produced ozone in water; hence the obvious need for an air compressor to overcome the hydrostatic load of the water tank.

C) In terms of the operating principle:

There are three methods of producing ozone in the laboratory [4] [6]:

I. Through electrical discharge (Corona effect);

II. Using ultraviolet radiation;

III. Cold plasma.

As a result there will be three types of ozone generators having operating principle based on one of the three methods.

The first method is applied in industry, research, and methods II and III are used in therapeutic work.

3. THE FACTORS WHICH INFLUENCE THE OZONE GENERATION

a) In the ozone generation, there is not only a single reaction, but the others complementary; for example, the nitrogen reacts with the electrons and forms a series of oxides (NO, NO_2).

Hence, the efficiency of ozone generation will be higher if the gas in which the discharge occurs is pure oxygen not air [7];

b) Water vapors influence these reactions; it is recommended that the gas discharge in which the discharge occurs (air or pure oxygen) is completely dry;

c) Ozone cannot be stored due its decomposition in time, it must be consumed when is produced.

The decomposition of nitrogen is more rapid as the temperature is higher; this requires adequate cooling of the ozone generator;

d) The ozone generation efficiency in a normal corona discharge and 60 Hz is 200 g/kWh at oxygen and 100 g/kWh at air.

It is noted that at the output of the ozone generator, there is no pure ozone, but a gas containing ozone; there are N_2, NO, NO_2.

In addition, the ozone production is dependent upon:

- The voltage between the electrodes;
- The absolute pressure of the air introduced into the ozone generator.
- The amount of generated ozone depends on the voltage and is higher if the voltage value is higher.

The amount of generated ozone is a function of air pressure and is much greater as the pressure is lower.

The amount of produced ozone, increase with the dry air flow rate; ozone flow rate increases with the enrichment of dry air with oxygen (up to 20% concentrations) [3].

4. ANALYSIS OF THE PRESSURE LOSS IN THE MICROBUBBLE GENERATOR

The microbubbles generator (MBG) is provided with 152 orifices with Ø 0.1 mm; the bubble emitted by the microbubbles generator is of micrometric dimensions and therefore the bubbles of air will be referred to as microbubbles.

To determine the water treatment plant scheme with ozone the pressure drop on the fluid circuit should be specified. The pressure loss when the gas flow (air or air with reduced content of nitrogen or oxygen enriched air in the cylinder) through the microbubbles generator is important.

The 152 orifices are parallel distributed; the pressure loss will be equal for each one.

Figure 1 shows a MBG scheme designed for determining the pressure loss of the MBG.

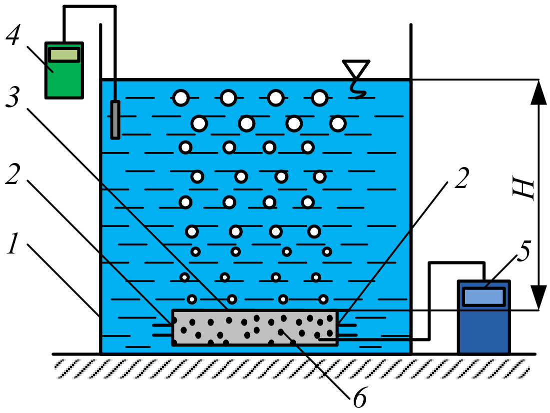


Fig. 1. Measuring scheme
1- water tank; 2 - compressed air inlet connection; 3 - orifice plate; 4 - thermometer with digital indication; 5 - manometer with digital indication; 6 - MBG body

The compressed air pressure from the tank (6) is p_1, and must overcome [8] [9]:

$$p_1 = p_H + \Delta p_{ts} + \Delta p_p \tag{5}$$

p_H - The hydrostatic load, H = 500 mm H_2O;

Δp_{ts} - Pressure loss to overcoming the surface tension;

Δp_p – The pressure drop that occurs when the air flows through the orifice at the dry plate.

From experimental measurements the following resulted [8]:

p_1 = 583 mm H_2O;

p_H = 500 mm H_2O.

The needed overpressure to form the bubble [9]:

$$\Delta p_{ts} = \frac{2\sigma}{R_0} \tag{6}$$

σ - the surface tension of water/air at 20 °C: $\sigma = 73 \cdot 10^{-3}$ N / m.

R_0 - the bubble radius at its detachment from the orifice plate.

Note: $D_0 = 2 \cdot r_0$ and $D_0 = 2R_0$; $d_0 = 0.1 \cdot 10^{-3}$ m; $\rho_l = 10^3$ kg / m^3.

$$R_0 = \frac{D_0}{2} \tag{7}$$

and the bubble diameter at its detachment can be calculated with [9]:

$$D_0 = \sqrt[3]{\frac{6 \cdot \sigma \cdot d_0}{(\rho_{H_2O} - \rho_{aer}) \cdot g}}\ [m] \tag{8}$$

The air density is determined from the equation of state [10]:

$$\rho = \frac{p}{RT} \quad kg/m^3 \tag{9}$$

$$\rho = \frac{10325 + 583 \cdot 9.81}{287 \cdot (20 + 273.15)} = 1.26 \quad kg/m^3$$

$$D_0 = \sqrt[3]{\frac{6 \cdot 73 \cdot 10^{-3} \cdot 0.1 \cdot 10^{-3}}{(10^3 - 1.26) \cdot 9.81}} = 0.00164 \quad [m]$$

$$R_0 = \frac{D_0}{2} = \frac{0,00164}{2} = 0,00082 =$$

$$= 0,82 \cdot 10^{-3} m$$

Equation (6) becomes:

$$\Delta p_{ts} = \frac{2\sigma}{R_0} = \frac{2 \cdot 73 \cdot 10^3}{0,82 \cdot 10^{-3}} = 178.04 \quad N/m^2 \tag{10}$$

$$\Delta p_{ts} = \rho_{H_2O} \cdot g \cdot \Delta h_{ts} \quad N/m^2$$

$$\Delta h_{ts} = \frac{p_{ts}}{\rho_{H_2O} \cdot g} = \frac{178,04}{10^3 \cdot 9.81} = 18,14 \cdot 10^{-3} \quad m \tag{11}$$

$$\Delta h_{ts} \approx 18,14 \quad mmH_2O$$

Equation (5) becomes:

$$583 = 500 + 18.14 + \Delta p_p \tag{12}$$

$\Delta p_p = 64.86$ mmH_2O

The first term on the right of equation (12) represents the overpressure necessary to overcoming the hydrostatic load, the second term to overcome the surface tension and the third term relates to the pressure required that an air bubble located in the tank with compressed air of the MBG to pass through the plate in the water volume.

If the hydrostatic load increases to 1000 mmH_2O, 2000 mmH_2O, a simple fan will not provide the injected gas overpressure.

As a result, at the water treatment tanks, swimming pools, etc., the scheme must contain an air compressor to provide the pressure losses on the gas system (air, ionized air, MBG).

5. SCHEMES OPERATING PRODUCTION FACILITIES OZONE

Because the water treatment basins have hydrostatic load of 2 ... 5 m, it is clear that in the injected gas into circuit must be a compressor.

The following provides two schemes:

A) Installation scheme to produce ozone from atmospheric air;

B) Installation scheme to produce ozone from air with low nitrogen content.

A) This scheme includes (Figure 2):

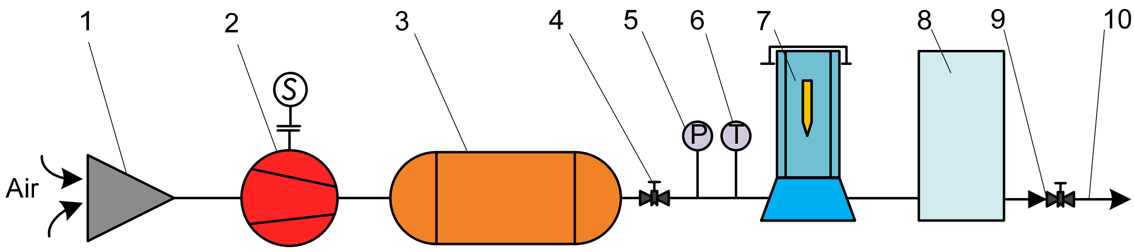


Fig. 2. Installation scheme to produce ozone from atmospheric air
1- air filter; 2- electro compressor; 3- compressed air tank; 4- compressed air flow rate regulating valve the; 5- pressure measuring device; 6- temperature measuring device; 7- flow meter; 8- ozone generator; 9- ozonized air flow rate control valve; 10-ionized air outlet connection

- an electro compressor injecting air through a flow meter (7) to the ozone generator (8); at the ozone generator output is ozonized air; the ozonized air is a mixed gas composed of N_2, NO, NO_2, O_2, O_3. The ozone concentration in the air is measured with a digital camera indication supplied by SC EUROVLAD SRL.

B) In this version, an installation for the production of ozone by using of an oxygen concentrator is considered.

In this case, in the ozone generator (8) in Figure 3 enters air composed of 95% N_2 and 5% O_2. The air with low nitrogen content is provided by the oxygen concentrator whose operating principle is based on the technique of zeolites as follows: at the concentrator (6) entrance there is compressed air and at the outlet there is nitrogen (N_2), which is released into the atmosphere and oxygen (95%) flowing towards the ozone generator (8).

In the fluid circuit there are:
- pressure measuring device (4);
- temperature measuring device (5);
- flow rate measurement device (flow meter) (7).

Obviously, introducing gas containing 95% O_2 in the ozone generator, the production of ozone (O_3) will be higher because there is no longer circulating nitrogen.

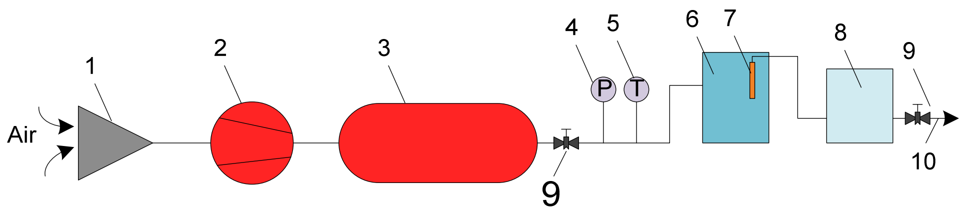


Fig. 3. Installation scheme to produce ozone using an oxygen concentrator.
1 - air filter; 2 - air compressor; 3 - compressed air tank; 4 - pressure measuring device; 5 - temperature measuring device; 6 - oxygen concentrator; 7 - flow meter; 8 - ozone generator; 9 - pressure and gas flow rate regulating valve; 10 - ozonized air outlet connection

6. THE USE OF OZONE

Ozone is used in the following fields [1] [9]:

1. In water treatment

In addition to decanters filters, etc., a drinking water treatment plant, wastewaters, etc., includes mixing chamber of the ozone with the water. Significant effects of the ozone use are:

- The bactericidal action; the degradation of organic substances; deactivating viruses; organoleptic qualities; discoloration; removing iron and manganese; destruction of toxic substances.

2. In the chemical industry

- Oxidation of unsaturated fatty acids and industrial-scale production of acids used in the manufacture of plasticizers, polymers with special features;
- Manufacture of nylon and polyester;
- The production of steroid hormones and vitamins.

3. In food industry

- Water treatment for beer and soft drinks preparation;
- Sterilizing bottles, packaging containers;
- Preparation of cultures of sulfite solutions resulting from the processing of pulp.

4. In pulp and textiles industry

- Bleaching agent in the pulp industry, instead of toxic and polluting chlorine;
- Improving technical characteristics of cellulose by the action of ozone;
- The ozone treatment makes the wool not to shrinks.

Technic-economical calculations show that using ozone for various technological applications not only provide superior performance, but in most cases it is even effective. For example, in the drinking water preparation 1-5 g ozone / m^3 is required depending on the pollution degree.

7. FRAMING THE OZONE GENERATOR IN A GROUNDWATER TREATMENT SCHEME

Water treatment uses ozone-enriched air by its production with the mentioned processes (paragraph 2). Depending on the water pollution degree, the treatment doses vary from 0.5 through 5 g O_3 / m^3.

The Water treatment station configuration depends on the nature of the fluid entering the station (groundwater, river water, polluted water, etc.) and its purpose: the production of drinking water, waste water to be discharged into the sewage system or in streams, rivers etc.

This paragraph aims to frame the ozone water treatment process in a functional scheme for groundwater. Groundwater containing dissolved gases and dissolved or suspended chemicals.

The general scheme will include (Figure 4) installations for:

- Groundwater capture;
- Gas elimination;
- Water oxygenation by introducing compressed air;
- Water filtration;
- Water disinfection by introducing O_3 using MBG.

If the polluted water contains bio-persistence organic or inorganic substances to be removed by chemical oxidation the following oxidation processes are used:

- Oxidation with the active oxygen (O), molecular oxygen (O_2), ozone (O_3), oxidation with hydrogen peroxide (H_2O_2);
- Oxidation with chlorine, with per acids, electrochemical oxidation.

In the case of oxidation with ozone, the ozone acts in two ways:

- As independently oxidizer losing an oxygen atom;
- By free radicals (OH) released in water.

The substances that can be destroyed or removed by ozonation are [1]:

- Completely destroy the proteins and amino acids;
- Removes iron and manganese;
- Removes phenols, hydrocarbons, detergents;
- Deactivates viruses and bacteria from water.

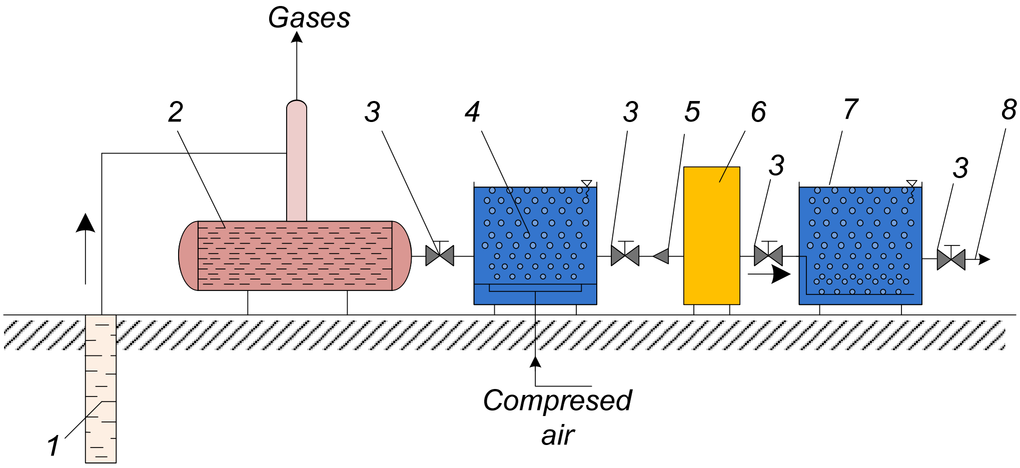


Fig. 4. The general scheme of framing the ozone generator in the groundwater treatment plant
1- capture probe; 2- degasser; 3 - the flow rate and fluid pressure control valves;
4- microbubbles generator (MBG); 5- filter; 6- ozone generator; 7- water ozonation tank;
8- the treated water outlet connection to the consumer

The operating diagram (Figure 4) has greater reliability, presents the moving parts and do not require constant supervision.

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