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Ozone Generation From Oxygen And Air: Discharge Physics And Reaction Mechanisms

U. Kogelschatz, B. Eliasson and M. Hirth

ASEA BROWN BOVERI
Corporate Research
5450 Baden, Switzerland

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Abstract

Industrial ozone generation uses a special high pressure, low temperature electrical discharge which is referred to as the dielectric barrier discharge or silent discharge. The filamentary structure of this discharge and the properties of individual microdischarges are discussed. The main reaction paths for the excited atomic and molecular species in oxygen and air are identified. Possible approaches to obtain high power densities, high ozone generating efficiencies or high ozone concentrations are discussed.

Introduction

During the past decade, industrial ozone generation has been improved in several aspects. Three areas of improvement can be clearly identified:

A. Higher power densities,

B. Higher ozone generating efficiencies,

C. Higher ozone concentrations.

The maximum power density (measured in kW/m^2 of electrode area) determines the total electrode area necessary to produce a required amount of ozone, and thus determines the size of the ozone generator. Today's medium frequency ozone generators reach power densities of 2-5 kW/m^2, which is considerably higher than the 0.2-0.5 kW/m^2 typical for the older 50/60 Hz ozone generators. This step has resulted in a drastic reduction in the size of ozone generating equipment with a corresponding reduction of investment costs. The ozone generating efficiency can be measured in kilograms of ozone produced per kilowatt-hour of electrical energy.

In the technical literature, the reciprocal value is preferred: the specific power consumption measured in kilowatthour per kilogram ozone produced. For many of the older installations, typical values were 10-25 kWh/kg. These values depend very much on the feed gas (air or oxygen) and on the desired ozone concentration. Modern ozone generators approach values of 10 kWh/kg in air and 4 kWh/kg in oxygen at low ozone concentrations. Much of this progress is due to a better understanding of the discharge physics and of the complex chemistry of ozone formation.

Microdischarge Properties

It is well established that the dielectric barrier discharge in air or oxygen at near atmospheric pressure is far from being homogeneous. The current flow through the discharge gap is brought about by a large number of statistically distributed microdischarges. The most striking manifestations of these microdischarges are Lichtenberg figures. Figure 1 shows the "footprints" of individual microdischarges on a photographic plate which was in contact with the discharge for a short time (about 1 millisecond).

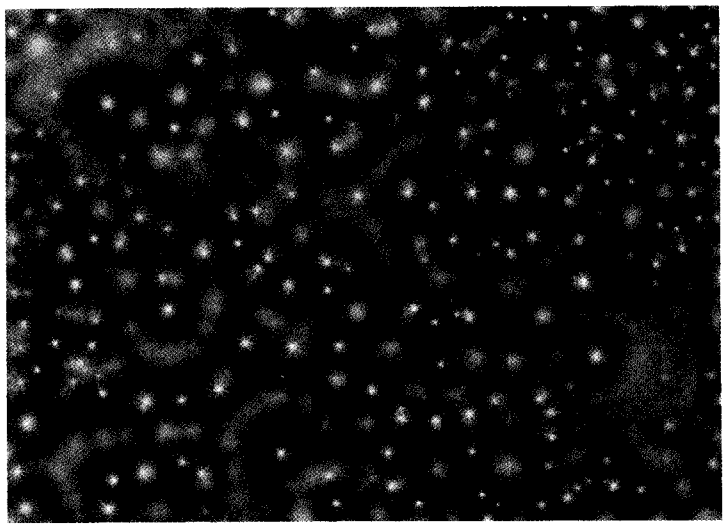

Figure 1. Photographic Lichtenberg figure showing the "footprints" of individual microdischarges (Original size: 7 cm x 10 cm).

More detailed information about these microdischarges was collected by fast image intensifier recordings (Tanaka et al., 1978; Heuser, 1985) and detailed current and charge measurements (Hirth 1979, Hirth et al., 1983). Since ozone is formed only in these microdischarges and not in the space between, it is essential to understand and optimize the conditions in the microdischarge channels. Today's understanding of the microdischarges can be summarized as follows:

Each microdischarge lasts only for a few nanoseconds (Figure 2), much shorter than was assumed in the older literature (Honda & Naito, 1955; Gobrecht et al., 1964).

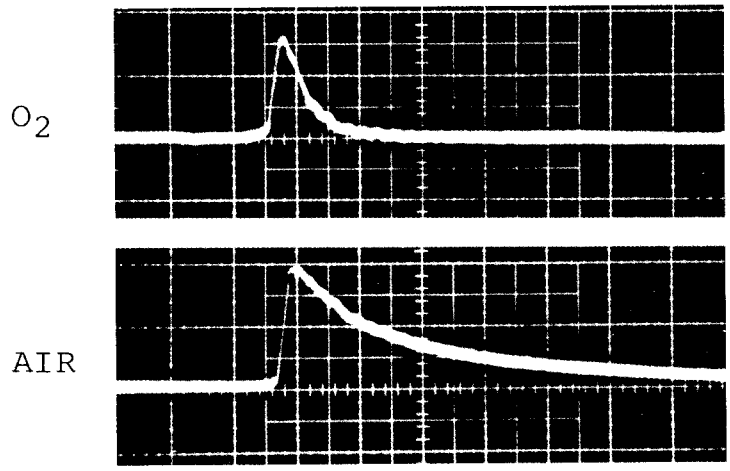

Figure 2. Microdischarge current in oxygen and in air (Amplitude: 40 mA/small division, time: 2 ns/small division).

The microdischarge has an almost cylindrical channel of roughly 100 μm radius and spreads into a much wider surface discharge on the dielectric. The current density in the microdischarge channel can reach values of 100-1000 A/cm^2. Due to the very short duration of microdischarges, the transported charge is of the order 10^{-10} - 10^{-9} coulomb, and its energy density is of the order 10 mJ/cm^3. The microdischarge channel can be considered as a transient glow discharge with electron temperature of approximately 50,000°K and gas temperature close to room temperature.

The efficiency of ozone production in such a microdischarge depends very much on its strength, which can be influenced by the gap spacing, the pressure, the dielectric, the properties of the metal electrode and, to some extent, also on the electrical circuit (pulsed ozone generators). Also, the humidity of the feed gas has a drastic effect on the microdischarge properties and on the chemical reaction paths. For this reason, the feed gas normally is dried to a dew point below -60°C.

Discharge Modelling

A volume element of feed gas travelling through the discharge gap will be exposed to a large number of microdischarges. The physical and chemical changes in a microdischarge channel can be treated by solving fairly complex reaction schemes (Gibalov et al., 1981; Eliasson et al., 1985; 1986a). When the breakdown voltage is reached, a very fast

ionization process generates the charge carriers necessary for current flow. In pure oxygen, O^+, O_2^+, O^-, O_2^-, and O_3^- ions are obtained in addition to electrons (Figure 3). Their relative importance depends on the strength of the microdischarge.

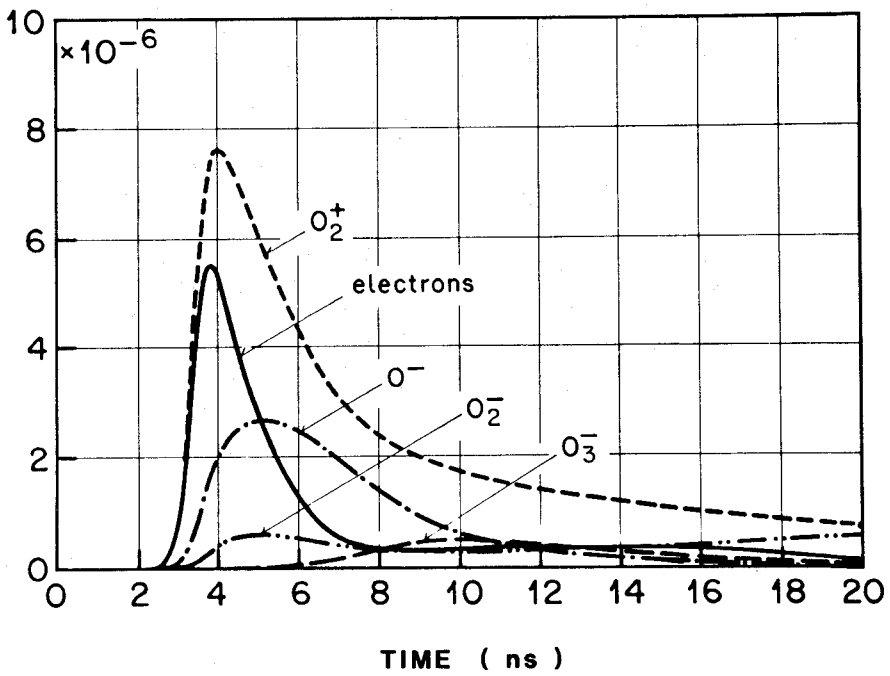

Figure 3. Numerical simulation of the charge carriers in a microdischarge channel. All particle densities are normalized to the gas density in the discharge gap (n_0 = 2.4 x 10^{19} cm^{-3}).

Also the partition of the discharge energy between electrons and ions depends very much on the strength of the microdischarge. In weak microdischarges, a considerable fraction of the energy is dissipated by ions. In stronger microdischarges, almost the entire discharge energy can be fed into the electrons.

The strength of a microdischarge can be characterized by the energy deposition in the microdischarge channel, or by the relative concentration of oxygen atoms ($[O]/[O_2]$) reached in the channel at the termination of the microdischarge. Recent investigations (Eliasson et al., 1985; 1986a) revealed that this quantity is several orders of magnitude higher than was assumed in previous publications (Yagi et al., 1979b; Gibalov et al., 1981). The strength of the microdischarge has an essential influence on the chemical reactions leading to ozone formation and the ozone generating efficiency.

Main Reactions In Oxygen

In a search for optimum conditions for ozone formation, a computer model treating 70 reactions among 16 particle species was used (Eliasson et al., 1986a). The main results of these calculations can be summarized as follows:

1) Ozone is formed mainly from oxygen atoms by the reaction:

$$O + O_2 + M \text{ ----> } O_3^* + M \text{ ----> } O_3 + M \qquad [1]$$

where M is a third collision partner (O_2, O_3, in air also N_2).

2) In pure oxygen the principal reactions resulting in oxygen atoms are:

$$e + O_2 \text{ ----> } e + O_2(A\ ^3\Sigma_u^+) \text{ ----> } e + O(^3P) + O(^3P) \qquad [2]$$

and

$$e + O_2 \text{ ----> } e + O_2(B\ 3\Sigma_u^-) \text{ ----> } e + O(^3P) + O(^1D) \qquad [3]$$

(The terms in brackets are spectroscopic notations used to characterize excited states of the atoms and molecules involved).

3) Ionic processes contribute only negligibly to ozone formation.

4) There is an optimum microdischarge strength for efficient ozone generation.

If the microdischarge is too weak, ions consume a considerable portion of the discharge energy, which thus is not utilized for ozone formation. On the other hand, the chemistry of ozone formation imposes an upper limit on the strength of the microdischarge. In very weak microdischarges, every oxygen atom leads to the formation of one ozone molecule, according to Reaction [1]. This no longer is true at higher oxygen atom concentrations, when additional reactions involving oxygen atoms gain importance. The main competing reactions are:

$$O + O + M \text{ ----> } O_2 + M \qquad [4]$$

$$O + O_3 \text{ ----> } 2\ O_2 \qquad [5]$$

$$O + O_3^* \text{ ----> } 2\ O_3 \qquad [6]$$

O_3^* stands for an excited transient ozone species which is the initial product of Reaction [1]. Figure 4 demonstrates that the ozone yield per oxygen atom, and thus the efficiency of ozone generation, drops drastically if the microdischarges become too strong. The optimum microdischarge strength is a compromise between avoiding energy losses to ions and still obtaining a reasonable conversion efficiency. It is of the order $[O]/[O_2] \sim 10^{-3}$.

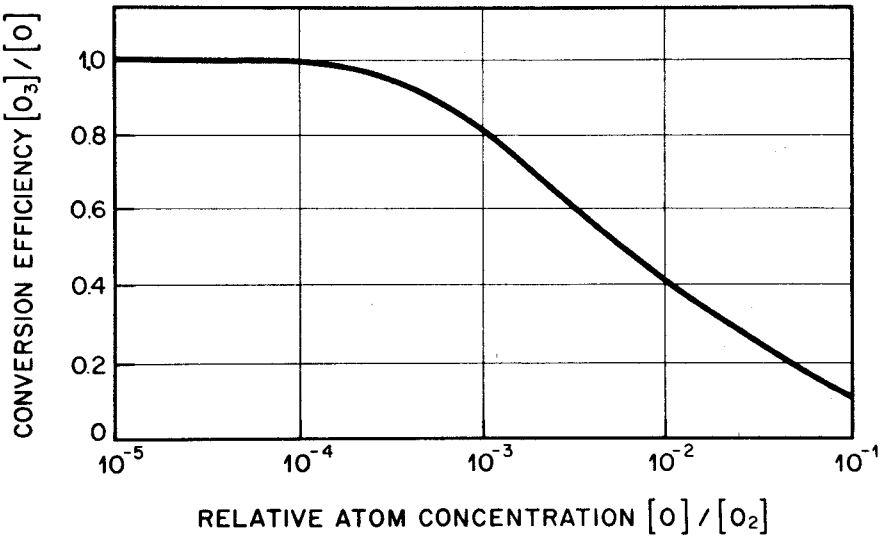

Figure 4. Number of ozone molecules formed per oxygen atom as a function of oxygen atom concentration.

Main Reactions In Air

Ozone generation in air is much more complicated than it is in pure oxygen. Additional ionic species (N^+, N_2^+) and the excitation and dissociation of nitrogen molecules adds to the complexity of the chemical reactions. Two striking experimental observations have been explained recently:

A. The presence of nitrogen apparently provides additional reaction paths for ozone formation;

B. At very high specific energies, the performance of the discharge changes in a drastic way -- namely, ozone formation breaks down completely, and all previously generated ozone is destroyed (state of discharge poisoning, ozone-less mode).

The clue to these phenomena is the presence of traces of nitrogen oxides that can be detected in the output of air-fed ozone generators. Measurements of the sum parameter $NO_x = NO + NO_2 + NO_3 + 2N_2O_5$ have been presented by different authors (Yagi et al., 1979a,b; Okazaki et al., 1988). More detailed measurements of the nitrogen oxides NO, NO_2, N_2O_5 and N_2O recently have been published (Gibalov et al., 1985; Kogelschatz & Baessler, 1986; Samoilovich & Gibalov, 1986). A paper on the detection of the last missing species, nitrogen trioxide (NO_3), was presented by Eliasson and Kogelschatz (1987).

The kinetics of NOx formation can be summarized as follows. The nitrous oxide N_2O and the nitric oxide NO are the initial oxides formed within

100 ns after the initiation of a microdischarge (Eliasson & Kogelschatz, 1986c). The main reaction leading to N_2O formation involves the metastable excited $N_2(A\ ^3\Sigma_u^+)$ molecule:

$$N_2\ (A) + O_2 \text{ ----> } N_2O + O \qquad [7]$$

Nitric oxide is produced mainly from two reactions involving nitrogen atoms:

$$N + O_2 \text{ ----> } NO + O \qquad [8]$$

$$N + O_3 \text{ ----> } NO + O_2 \qquad [9]$$

Reaction [8] results in additional oxygen atoms that can finally form ozone.

There are two more such additional reactions paths (Eliasson et al., 1984):

$$N + NO \text{ ----> } N_2O \qquad [10]$$

$$N_2\ (A,B) + O_2 \text{ ----> } N_2 + 2\ O \qquad [11]$$

In the presence of ozone and oxygen atoms, NO is oxidized via NO_2 and NO_3 to the highest oxidation state N_2O_5. There are many reaction paths among the different nitrogen oxides. The complexity of the NO_x kinetics is demonstrated by Figure 5, which shows a numerical simulation of the action of a series of 400 identical microdischarges in a mixture of 80% N_2 and 20% O_2 (Eliasson & Kogelschatz, 1987). The reaction scheme treats 143 chemical reactions among 30 reacting species, and can simulate the major experimental trends of ozone and NO_x formation in air. Apparently the state of discharge poisoning, in which ozone formation breaks down, can be predicted by such a model also.

Conclusion And Engineering Aspects

Understanding of the ozone formation process in oxygen and in air has improved considerably during the last decade. Detailed experimental investigations into the properties of microdischarges, exact measurements of ozone and different NO_x species under different operating conditions, and computer modelling of the various processes in the discharge gap have led to an almost quantitative understanding of the major processes. It turns out that these investigations are not only of scientific merit, but also have an essential influence on the engineering of advanced ozone generators. The conditions in the microdischarges can be influenced and controlled by the composition of the feed gas, the gap spacing, the pressure, the dielectric, the metal electrode, the power supply, and the cooling circuit. Today, we are in a position to tailor an ozone generator to the needs of the customer.

The overall parameters: power density, efficiency and high ozone concentration are, in certain respects, conflicting requirements. The best

compromise depends on the specific application. The requirements for ozone in drinking water or waste water treatment may be quite different from the requirements of ozone users in the chemical or pharmaceutical industries, or when ozone is used for bleaching kaolin or paper pulp.

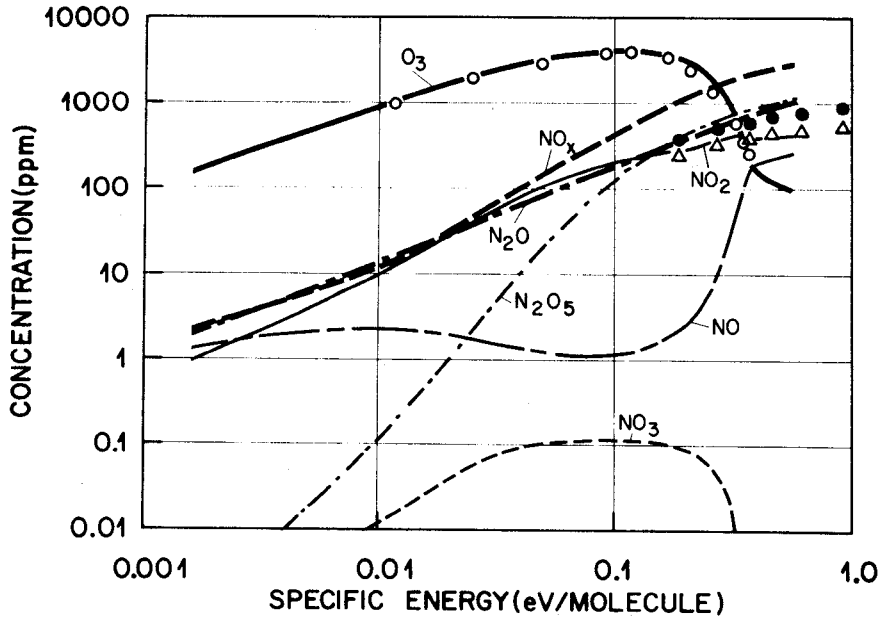

Figure 5. Comparison of calculated and measured ozone and nitrogen oxide concentrations. Assumptions: Energy per microdischarge: 5.4 mJ/cm^3; time between microdischarges: 3 ms. Measurements: o ozone, NO_x, Δ N_2O.

Every ozone generator with fixed operating conditions can be characterized by its efficiency versus concentration curve. As Figure 6 shows, with proper engineering, we do have quite a bit of influence on this curve. If high efficiencies at low concentrations are demanded, an ozone generator performing according to curve I would be the choice. If a certain application requires very high ozone concentrations, we would certainly prefer an ozone generator which performs according to curve II. Concentrations as high as 6% (by weight) in air or over 20% in oxygen can be reached. Although this last value is higher than the explosion limit given in the literature (13-17% ozone by weight in oxygen), we have never observed explosive instabilities in our laboratory experiments.

For larger ozone generating systems, a careful evaluation of the composition and preparation of the feed gas, type of ozone generator, handling of process gas (once-through or recycling) will be necessary to specify the best system parameters. It has been a long way from the first investigations into the nature of microdischarge properties to the engi-

neering of large ozone generating plants. The performance of today's advanced ozone generating systems certainly proves that it was worth the effort.

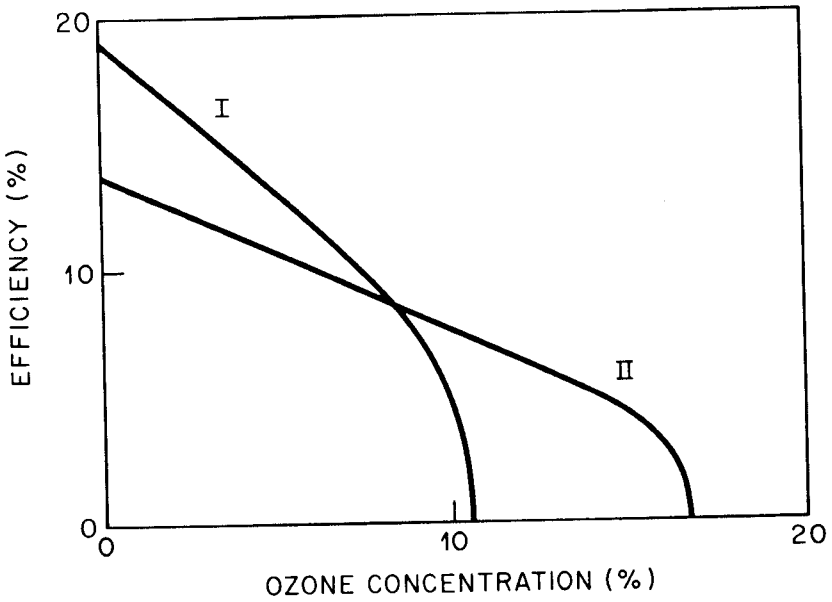

Figure 6. Efficiency versus concentration characteristics of different designs of ozone generators (100% efficiency corresponds to a specific power consumption of 0.82 kWh/kg).

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Key Words

Ozone, Ozone Generation From Oxygen & Air, Discharge Physics of Ozone Generation, Reaction Mechanisms of Ozone Generation, Generation of Nitrogen Oxides During Ozone Generation From Air, Engineering Aspects of Ozone Generation

Résumé

La production industrielle d'ozone requiert l'utilisation d'une décharge électrique spéciale à haute pression et basse température: la décharge silencieuse. La structure de cette décharge et les propriétés des micro-décharges élémentaires sont ici présentées. On identifie les principales voies de réactions pour les divers atomes et molécules excités dans l'oxygène et dans l'air. On expose les possibilités d'obtenir de hautes

densités de puissance, des rendements élevés de production d'ozone ou des concentrations élevées d'ozone.

Zusammenfassung

Die industrielle Ozonherstellung basiert auf einer speziellen Hochdruck-Niedertemperatur-Gasentladung: der stillen Entladung. Die Filamentstruktur dieser Entladung und die Eigenschaften einzelner Teilentladung werden diskutiert. Die wichtigsten Reaktionspfade für die verschiedenen angeregten Atom- und Molekülzustände werden sowohl im Sauerstoff als auch in Luft identifiziert. Ferner werden Möglichkeiten zur Erreichung hoher Leistungsdichten, hoher Wirkungsgrade oder hoher Ozonkonzentrationen diskutiert.