THE INFLUENCE OF THE VOLTAGE WAVE ON THE FORMATION OF OZONE

J. Salge and P. Braumann
Institut für Hochspannungstechnik, Technische Universität Braunschweig,
Postfach 3329, 3300 Braunschweig, Federal Republic of Germany

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ABSTRACT

An improvement in the efficiency of ozone formation is demonstrated by applying fast rising voltages to an ozonizer. A close correlation between the discharge current wave-shape and the production of ozone is observed. The current wave is strongly influenced by the rise time and the amplitude of the voltage. By applying voltages with short rise times it is possible to increase the gap distance between the electrodes and to use discharges between two metal electrodes only. Multi - pointed earth electrodes were found to be advantageous. Photometric measurements show a maximum of ozone formation rate at the dielectric surfaces.

1. INTRODUCTION

Appreciable quantities of ozone can be produced only by gas discharges /1/. Hosselet has proposed voltages with short rise and fall times /2,3/, and by periodic charging and discharging an ozonizer with a small time constant he demonstrated, its efficiency can be improved. To apply these promising results to practical devices more information about the fundamental principles is required and in particular a relation between the discharge characteristic and the ozone formation process has to be found. By applying fast rising voltages it is furthermore of interest to find out whether other electrode configurations will enable the efficiency to be improved. To give an answer to these important questions basic experiments have been carried out on an ozonizer, which allowed a variation of the above mentioned parameters.

2. BASIC CONSIDERATIONS

Before discussing the results of the experiments, it is useful to consider the fundamental processes, which occur when an ozonizer is supplied with different voltage waves. Fig. 1 shows a schematic diagram of an ozonizer. The discharge gap (1) is formed between one electrode (4) and a solid dielectric (3), arranged close to the second electrode (2). Before the breakdown of the discharge gap (1) the voltage distribution is determined by the capacitances of the two partial gaps, (1) and (3). When the discharges take place oxygen atoms are generated in the gap by collision processes between accelerated electrons and oxygen molecules. After this ozone is formed by the attachment of these atoms to the oxygen molecules. In order to get a sufficient ozone production a homogeneous distribution

of the discharge processes in the whole gas volume would appear to be of significant importance /4,5/. At slow rising voltages the conditions are such that only a limited number of simultaneous single discharges will occur. But with voltages having short rise times - i. e. rise times in the range of the discharge development time - the conditions for a simultaneous development of discharges are greatly improved /6/. These considerations show, that by supplying an ozonizer with fast rising voltages a more efficient production of ozone is to be expected.

3. EXPERIMENTAL ARRANGEMENT

Fig. 2 shows the ozonizer used for the experiments. Its upper part comprises the high voltage electrode (1) and the solid dielectric (2), which was made of glass or alternatively of epoxy resin (EP). In both cases the thickness was 2 mm. (EP proved to be sufficiently reliable for the experiments). The dimensions of the rectangular brass earth electrode were 84 x 64 mm^2. The gap distance s between the dielectric surface and the earth electrode was variable from 2 to 12 mm. No cooling of the ozonizer was provided.

In fig. 3 a simplified diagram of a circuit to generate rectangular voltages together with a schematic voltage shape is given. The ozonizer is switched alternately by the triggered spark gaps, FS1 and FS2, to the capacitors C_{S1} and C_{S2}. These were charged to opposite polarity, resulting in a maximum voltage difference across the ozonizer of ΔU = 60 kV. The range of the voltage rise was in the order of 2 kV/ns and could be reduced by the resistor R_1.

4. RESULTS

4.1 DISCHARGE CHARACTERISTIC

In fig. 4 the voltage and the corresponding current wave (b) in a typical experiment are given together with the equivalent circuit diagram (a). C_3 represents the capacitance of the solid dielectric, C_2 the capacitance of the discharge gap and R_2 the ohmic resistance of the discharge. The distance s of the gap was 6 mm. The voltage u_1 across the ozonizer was measured by means of a capacitive damped voltage divider /7/ the current i_1 by a coaxial foil resistor of very small time constant /8/. The voltage u_2 and the current i_2 are calculated from u_1 and i_1 /9/.

The voltages u_1 and u_2 caused by the previous discharge, are negative at t_o. During the time interval t_o - t_1 the charge of the ozonizer is reversed by the rising voltage u_1. At t_1 the discharge starts with a rapidly increasing current i_2. The electric field strength then has a value of 4.5 kV/mm. During the discharge the capacitance C_3 of the solid dielectric is being charged, indicated by the increasing current i_1. This charging process caused a collapse of the voltages u_1 and u_2, and of the current i_2. The discharge is interrupted after about 20 ns.

If the risetime of the applied voltage is decreased only by a factor of 10 a fundamental change of the discharge characteristic was observed. In this case the duration of the discharge period is extended due to the larger rise time of the voltage, and a greater number of much smaller current pulses occur, as in ozonizers operated by a sine wave of mains frequency. Their amplitude is reduced by two orders of magnitude compared

with that shown in fig. 4. These results agree with the considerations discussed above.

A change of the discharge current was also found, if the voltage u_1 had been increased with a constant gap distance s. Both the duration was exended and more than one current pulse was observed.

Furthermore experiments with fast rising voltages have shown that current and voltage shapes similar to those of fig. 4 can be achieved for gap distances up to 12 mm. The expected homogeneity of the discharges is confirmed by corresponding time integrated photographic records. These show a nearly homogeneous glow distributed over the whole discharge volume. Concentrated bright isolated discharges, observed when the ozonizer is energized by sine wave of power frequency, are no longer seen. A further improvement is achieved by using a multi-pointed electrode, as shown in fig. 5. In this case the gap distance could further be increased up to 25 mm without influencing the homogeneity of the discharge.

Moreover the generation of homogeneous discharges can be maintained between two metal electrodes when the oxygen is mixed with nitrogen, for instance with a ratio of three parts of oxygen to one part of nitrogen. In this case the function of the solid dielectric material is done by a closely coupled capacitor in series.

4.2 OZONE PRODUCTION

To demonstrate the relation between the discharge characteristic and the ozone production the amount of ozone generated per kWh, yield A_W, is plotted in fig. 6 against the ozone concentration G for different voltages and gap distances. The increase of G was achieved by increasing the voltage. The maximum voltage level is limited by the breakdown field strength of the solid dielectric (glass). The ozonizer (fig. 2) was operated at 1 bar at room temperature with pure oxygen of a dew-point lower than-60°C with a constant gas-flow rate of 110 l/h. No additional cooling was provided. The ozone concentration was measured photometrically at a wavelength of 254 nm (extinction coefficient 3024 l/(Mol cm) /10/. For rectangular voltages the electric energy input was determined by the product of the charging voltage U_L on C_{S1} and C_{S2}, shown in fig. 3, and the integral of the current i_1 through the ozonizer. These values include all losses in the ozonizer and its connections to the energy source, and in particular the losses of the switching spark gaps. An estimation shows that they are in the range of 30-40% of the total energy input /9/. For sine wave voltage the energy input was determined by the Schering-Bridge-Method /11,12/.

Curve 3 plotted in fig. 6 shows a decrease in the yield A_W with increasing ozone concentration G, when the gap distance is 2 mm, and the ozonizer is supplied with fast rising voltage fronts with a repetition rate of 10 ms. Curve 1 gives the results, when the ozonizer is supplied with a sine wave voltage of 50 Hz. A comparison between curve 3 and curve 1 shows for a constant concentration G a higher yield A_W is obtained, when fast rising voltage fronts are applied. On the other hand at a constant yield A_W, that means at the same efficiency, a higher concentration G is given. This demonstrates the gain derived from the rectangular voltage.

This becomes more evident at gap distances of 6 mm. Fast rising voltages are then found (curve 4) to give a considerable gain in both yield A_W and concentration G, whereas a drastic deterioration is observed for sine wave voltages (curve 2). With fast rising voltages the replacement of the plane earth electrode by a multi-pointed electrode results in the optimum performance, shown by curve 5, which relates the maximum yields A_W to concentrations G. Thus for nearly constant yields A_W the ozone concentration G can be increased by factors of between 3 and 5. Probably this improvement is due to the reduced average field strength across the discharge gap, to the better cooling conditions resulting from the enlarged electrode surface and also to the more homogeneous discharge distribution obtained by the multi-pointed configuration. There is no fundamental change, if the gas flow rate is reduced. Experiments at low flow rates have clearly shown that the difference between both excitation modes becomes more evident.

Another important dependence is shown by fig. 7. This gives the ozone yield A_W plotted against the rectangular voltage ΔU applied to the ozonizer with gap distances of 2 and 6 mm respectively. The experimental parameters are given in the figure. Shortly after the voltage has reached a value, sufficient to cause a discharge in the ozonizer, there exists a maximum yield for both gaps. The decrease of the yield A_W with increasing voltage ΔU means, that the ozonizer is not able to utilize as much of the total energy supply in the formation of ozone. The main change caused by the increased voltage is the extended duration of the discharge current, while the average field strength across the discharge gap remains almost constant. The results indicate furthermore that to achieve high efficencies the energy per volume in a single discharge period should be kept as small as possible. Therefore in order to get large ozone concentrations the discharge periods should be multiplied.

4.3 SPATIAL OZONE FORMATION

Finally to investigate the spatial ozone development a beam of radiation of a wave length of 254 nm, 0.5 mm Ø, was directed through the discharge volume at different positions. The experimental arrangement together with the results of a typical experiment are given in fig. 8. Here the time dependent development of the local ozone concentration at the surface of a glass dielectric (1) and a plane brass electrode (2) is plotted in relation to the applied voltage given diagrammatically. At the start of the experiment the discharge volume contained pure oxygen at 1 bar. The gas flow was zero. Each increase of the concentration G corresponds to a voltage front. Between two voltage fronts a slow decrease in concentrations is observed due to local differences. During the whole observation period of 160 ms the concentration G increases linearly without any saturation effects.
Comparing the concentration development of the two positions a drastic difference of G is seen. The local concentration is much greater at the surface of the glass dielectric than at the metal electrode. This is in agreement with the experimental results on ozonizers supplied with sine wave voltages by MC Inally /13/, but up to now no reasonable explanation has been given for this phenomenon.

Additional measurements conducted at a higher time resolution showed a

long delay of approximately 10 - 20 µs between the pulse discharge and the development of the maximum ozone concentration. This is in good agreement with experiments of Hochanadel e. al. /14/ and theoretical considerations by Eliasson e. al. /15,16/.

5. CONCLUSIONS

The investigations have demonstrated clearly the gains that can be realized in the discharge process and the formation of ozone in an ozonizer by the use of fast rising voltages. Similar results were recently published by Rosocha e. al. /17/. With voltages rising at a rate of 2 kV/ns an improved homogeneity of the discharges was achieved. This results in both an increased ozone yield and an increased ozone concentration. In contrast with ozonizers supplied by sine wave voltages a further improvement was observed by increasing the distance of the discharge gap. An additional improvement was achieved by using multi-pointed electrodes.
The experiments were conducted on a small ozonizer. It is an open question as to how the requirements can be met by larger devices. To achieve fast rising voltage fronts in ozonizers some orders of magnitude larger, high currents must be handled at high power levels. The main aim of current investigations is to find practicable and reliable technical solutions to these problems.

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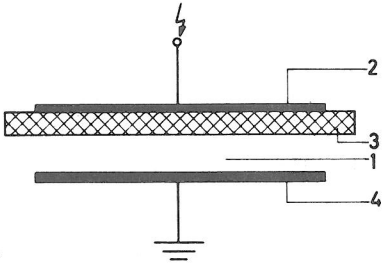

Fig. 1 Schematic diagram of an ozonizer: (1) discharge gap, (2) high voltage electrode, (3) solid dielectric (glass), (4) earth electrode

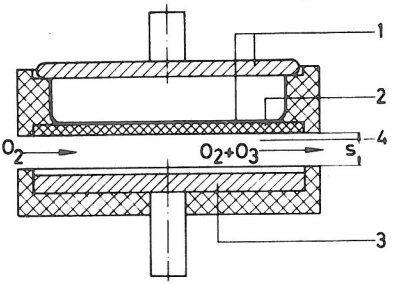

Fig. 2 Ozonizer: (1) high voltage electrode, (2) solid dielectric (glass or epoxy resin), (3) earth electrode, (4) discharge gap, gap distance s

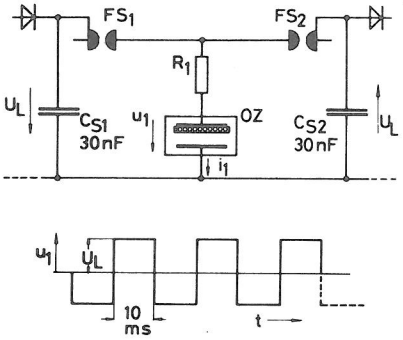

Fig. 3 Circuit diagram for the generation of rectangular voltages, OZ: ozonizer, FS_1, FS_2 triggerable spark gaps, voltage wave schematic

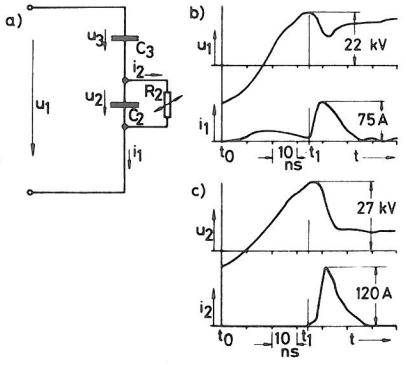

Fig. 4 (a) Equivalent circuit diagram of an ozonizer,
(b) voltage wave u_1 across the ozonizer and corresponding ozonizer current i_1,
(c) computed discharge gap voltage u_2 and discharge current i_2,
C_3=58pF (solid dielectric, EP), C_2=8pF (gas gap), R_2: ohmic resistance of the discharge, s=6mm

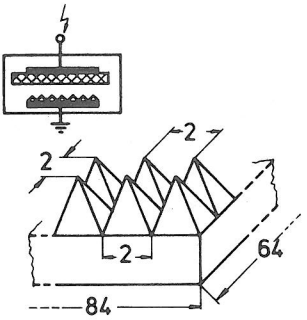

Fig. 5 Multi-pointed elektrode

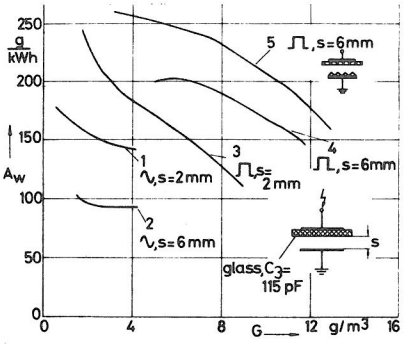

Fig. 6 Ozone yield A_W against concentration G for different voltages (f=50 Hz) and gap distances s, pure oxygen at 1 bar, gas flow rate 110 l/h

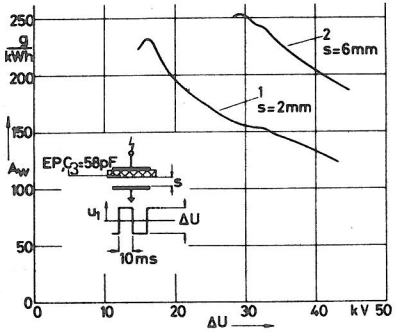

Fig. 7 Ozone yield A_W against the voltage ΔU with gap distances of 2 mm and 6 mm, plane earth electrode, gas flow rate 110 l/h

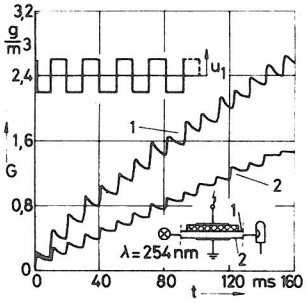

Fig. 8 Time dependent development of the local ozone concentration (1) at the surface of the glass dielectric (C_3=115pF) and (2) at the plane brass electrode, voltage wave schematic, U_L=20kV