TOWARDS A POSSIBLE INDUSTRIAL PRODUCTION OF OZONE WITH AN ELECTRON-BEAM-CONTROLLED DISCHARGE

G. Fournier, J. Bonnet, J. Fort, D. Pigache
Office National d'Etudes et de Recherches Aérospatiales
92320 Châtillon - FRANCE

and M. Lécuiller
LPD (ER 114 du CNRS) Ecole Supérieure d'Electricité
Plateau du Moulon, 91190 Gif-Sur-Yvette - FRANCE.

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ABSTRACT

The possibility to use an electron-beam-controlled discharge as an industrial ozonator is considered. At a pressure of 1,15 bar, an efficiency of 4.6 Wh/g is achieved at low ozone fraction ($3.8\ 10^{-4}$). Predictions of a numerical model are in semi-quantitative agreement with experiment. The discussion suggests that some important assumptions and some basic data can be better appraised.

1 - INTRODUCTION

It was demonstrated by the authors that an electron-beam-controlled discharge could be used as an efficient industrial ozonator [1]. The oxygen pressure in the preliminary experiments [1] was limited to 0.4 bar. The first step towards an industrial application for water purification requires an operation pressure a little greater than 1 bar. The second step is the demonstration of a good synthesis efficiency at low ozone concentration. The achievement of both these steps is reported in this paper. A milestone on this way is a substantial increase of the beam current density with respect to former experiments.

The third step would consist in the demonstration of a competitive efficiency at the higher concentration required for industrial application.

The experimental results are discussed and compared with the predictions of a numerical model.

2 - EXPERIMENTAL ARRANGEMENT

The electron beam controlled discharge is a classical arrangement [1] schematically drawn in figure 1. The kapton electron window is 5 x 15 cm and the discharge gap is a few centimeters. Pure oxygen at about 1 bar is flown through the active region with a rate of 13.7 l/mn (STP). The energy of the electron beam is 100 keV and its density J_b can be varied up to 8 mA/cm^2. Better results are obtained when the massive electrode is used as a cathode.

The discharge voltage is continuously applied and the beam is pulsed. Repetitive pulse operation is investigated.

The ozone fraction is measured by two different means, both outside of the discharge chamber. The optical transmission $\mathcal{T}$ at 255 nm gives an ozone fraction c

$$(1) \qquad c = -0.38 \ \text{Log} \ \mathcal{T}/1000\ p$$

for a pressure p in bars at a temperature $T = 298$ K. Iodine dosimetry is in excellent agreement with spectrometry [2].

3 - EXPERIMENTAL RESULTS

Two cases of operation, which are significant for possible future applications, are chosen for discussion. Their conditions are given in Table I. The case with beam alone and that with beam + discharge have comparable average power. For the short pulse operation (beam + discharge), the oscillogram is given in figure 2. It can be seen that the authors choose to define the pulse length from 80 % the steady state value to the beginning of cut-off. The reason for this is that the discharge is effective with respect to oxygen dissociation (which drives O_3) only for higher current as it will be shown later. Obviously, there is some conflict between the estimates deduced from this assumption and the actual conditions of a slowly cutting electron gun : The authors think that the figure they give for the efficiency is more significant for an appraisal of the application promises than the one they do obtain with the present device if the whole pulse is taken into account.

PROPERTIES	CASE 1 BEAM ALONE	CASE 2 BEAM + DISCHARGE
Pressure (bar)	1.15	1.15
Temperature (K)	298	298
Beam current density (mA/cm^2)	3.7	8
Pulse length (μs)	100	16
Beam energy (J)	2.8	0.96
Repetition rate (Hz)	1.43	0.8
Discharge gap (cm)	4	2
Discharge voltage (kV)		20.1
Ratio {electric field/gas density} (Vcm^2)		$3.6\ 10^{-16}$
Discharge current (A)		9
Energy input (J/l, STP)	8.8	6 from the beam 18 from the discharge
Average power (W)	4	3.08
Ozone fraction	$2.6.10^{-4}$	$3.77.10^{-4}$
Efficiency of ozone production (Wh/g)	8.8	4.6

TABLE 1 - PHYSICAL PROPERTIES OF TWO OPERATION CASES CHOSEN FOR DISCUSSION

The temperatures given in table I are measured in the pipe at the exit

of the discharge chamber. It should be noted that moderate temperature variations (≃ 20 K) occur during discharge operation and that important temperature gradient (≃ 100 K) are present continuously inside the chamber. If the gas temperature in the discharge is close to 400 K rather than to 298 K, the value of the ratio E/N (electric field/gas density) should be shifted to about 4.8 10^{-16} Vcm^2.

4 - NUMERICAL MODEL AND DISCUSSION

A - Effect of an electron beam alone on oxygen - The range of a 100 keV beam under the conditions given in table I is about 12 cm. For a gap of 4 cm, the energy fraction deposited in the gas is approximately.35 times the beam energy, that is 1 J, if backscattering of high-energy electrons on walls and massive electrode is neglected.

The energy branching ratios for the various processes involved in electron-beam-oxygen interactions are computed with a code [3] based on a discrete solution of the Boltzmann equation. The cross sections for this code are analytical approximations of Watson et al. [4] and some complements from Phelps et al. [5,6] for processes for which no equation is given in [4] . An energy fraction of 0.32 % is transferred to dissociative attachment at 4.4 eV and 6.78 % goes to dissociative excitation at 8.4 eV. If only these processes yield oxygen dissociation [5], the average dissociation frequency for case 1 is 7.8 10^{16} s^{-1}.Dissociative attachment gives one oxygen atom since O^- makes rapidly O_3^- with O_2. Dissociative excitation at 8.4eV gives two oxygen atoms (the one produced in the ^1D state loses its energy with O_2 to make rapidly a $b^1\Sigma_g^+$ metastable [5]). The resulting ozone fraction is 0.23.10^{-4} to be compared with a measurement of 2.6 10^{-4}. Obviously, the ozone source (loss is neglected) is underestimated with this assumption.

On the other hand, if it is assumed that the excitation processes at 4.5 and 6 eV are dissociative, it is found that the discrepancy factor is about 3. This factor would still be slightly reduced if beam backscattering was taken into account. However, a correction of the cross sections for dissociation would be necessary in any case.

B - Effect of the discharge - An usual Boltzmann code is used with Phelps'cross section data [5,6] for every process. At E/N = 3.6 10^{-16} Vcm^2 in 1.15 bar of oxygen, the electron attachment rate is found to be [3.5 10^{-12} (3 body attachment) + 2.1 10^{-11} (dissociative attachment)] that is 2.5 10^{-11} cm^3/s. The ionization source term under the conditions of case 2 is about 1.3 10^{19} cm^{-3}/s (beam backscattering neglected) and this results in an electron density of 1.9 10^{10} cm^{-3} and in an electron current density of 25 mA/cm^2. All the ions are assumed to have the same mobility, 2.15 cm^2 V^{-1} s^{-1} [7] and the same recombination coefficient of 2 10^{-6} cm^3 s^{-1} under the present conditions [8] . The ion density and the total ion current density are then estimated to be 2.5 10^{12} cm^{-3} and 17 mA/cm^{2}respectively. The total discharge current predicted by this estimate is then 42 mA/cm^2 or 3.2 A to be compared with 9 A in the experiment (case 2). This discrepancy is large with respect to the reasonable assumptions used and it is clear that experiment and calculation should be developped in order to assess the validity of the various data and assumptions. However, it should be noted that the order of magnitude of the electron current is at least as large as that of the ion current. This is an imperative condition to have an efficient ozonator since only electrons convert electrical energy into oxygen dissociation (and then into O_3). As the electron current grows as j_b whereas the

ion current varies with $j_b^{1/2}$, this condition can only be obtained with sufficient electron beam currents.

If it is assumed that oxygen dissociates only via dissociative attachment at 4.4 eV and excitation at 8.4 eV [5], the production rate of atomic oxygen as given by the Boltzmann code is 3.41 10^{-11} cm^{-3}/s at $E/N = 3.6\ 10^{-16}$ V cm^2. The dissociation effect of the beam is not taken into account in this first estimate and it will be discussed later. If there is no ozone loss other than the gas flow and if all atomic oxygen is converted into ozone, the average value of the ozone fraction downstream the discharge chamber should be 5.3 10^{-6} for a 16 µs pulse (or 8 10^{-6} if the total pulse length is taken into account). This value of 5.3 10^{-6} is refered to as c_o and will be used as a reference in the continuation of the discussion. Here the discrepancy with the experiment (3.8 10^{-4}) is of the order of 50 to 70. A tentative explanation of this discrepancy can be discussed as follows :

1) An upper limit to the participation of the electron beam in oxygen dissociation can be obtained if the effect of the beam alone is simply added to the effect of the electric field. The computation with the assumption that the beam dissociates only via dissociative attachment (4.4 eV) and excitation at 8.4 eV gives an ozone fraction of about 0.36 c_o to be added to that produced by the electric field. However, it has been demonstrated in part 4.A that this estimate should be multiplied by a factor of about 10 to agree with the experimental results. Then the upper limit of the beam effect on ozone fraction could be about 3.6 c_o.

2) A comparison with conditions of lower excitation of the medium [5] suggests that under the present conditions, the 4.5 and 6 eV excitation processes could be dissociative. With this assumption, the production rate of oxygen atoms is 7.3 10^{-10} cm^3/s and the predicted ozone fraction is 21.4 c_o.

3) An alternative consists in a suggestion according to which a three body reaction involving two $b^1\Sigma_g^+$ metastables would convert these metastables into ozone [9]. The generation rate for $b^1\Sigma_g^+$ can be obtained by adding to direct excitation the rates for 4.5, 6 and 8.4 eV processes, the energy of which cascades on $b^1\Sigma_g^+$ [5]. This total rate is 4.7 10^{-10} cm^3/s and the corresponding ozone fraction could be 6.9 c_o.

4) The effect of possible non uniformities which change the ratio E/N (electric field/gas density) is much less than the discrepancy to be explained.

Assumptions 2) and 3) cannot be added : Energy cascading from the main excitation processes (4.5 and 6 eV) is only possible if no dissociation occurs. Assumption 2), that is dissociation after 4.5 and 6 eV excitation gives a better appraisal and seems much more likely than assumption 3). Starting from the ozone fraction it gives, that is 21.4 c_o, the addition of the effects labelled 1) and 4) brings only a moderate correction. At last, if a fraction of the discrepancy about the discharge current is devoted to a false estimate of the electron density, the final prediction is not too far from the measured value.

5 - CONCLUSION

An electron beam controlled discharge is capable of ozone generation in pure oxygen with an efficiency of 4.6 Wh/g at 1.15 bar. Up to now the ozone

fraction is low ($3.77\ 10^{-4}$) and attempts to increase it to a value relevant of industrial application with a satisfactory efficiency have been unsuccessful in the present reactor. The difficulty seems to be related to a lack of control of gas temperature.

New experiments and an available code for heavy particles kinetics should permit a complete understanding of the ozone production process in an electron beam controlled discharge.

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REFERENCES

[1] - G. Fournier, R. Lucas, D. Pigache and M. Lécuiller,
Proc. 3rd Int. Symp. on Plasma Chemistry, Limoges, July 13-19, 1977.

D. Pigache, G. Fournier, R. Lucas and M. Lécuiller,
Proc. 13th Int. Conf. on Phenomena in Ionized Gases, Berlin, Sept.12-17,1977.

[2] - Iodine dosimetry was performed by Sté Degrémont.

[3] - G. Fournier, J. Bonnet, J. Bridet, J. Fort and D. Pigache,
Proc. 14th Int. Conf. on Phenomena in Ionized Gases, Grenoble,
July 9-13, 1979.

[4] - C.E. Watson, V.A. Dulock Jr., R.S. Stolarski and A.E.S. Green,
J. Geophys. Res., 72, 3961 (1967).

[5] - S.A. Lawton and A.V. Phelps,
J. Chem. Phys., 69, 1055 (1978).

[6] - A.V. Phelps,
Cross Sections of 11/3/1977, private communication.

[7] - R.M. Snuggs, D.J. Volz, J.M. Schummers, D.W. Martin and E.W. McDaniel,
Phys. Rev. A3, 477 (1971).

[8] - S. Mc Gowan,
Can. J. Phys. 45, 439 (1967).

[9] - G. Fournier, R. Lucas, D. Pigache and M. Lécuiller,
Bul. Am. Phys. Soc., 23, 146 (1978).

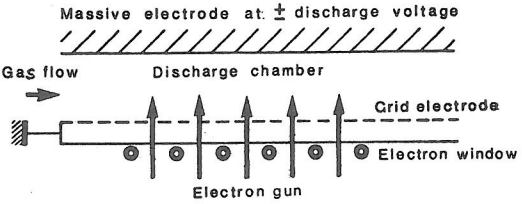

Figure 1 - Experimental arrangement (schematic)

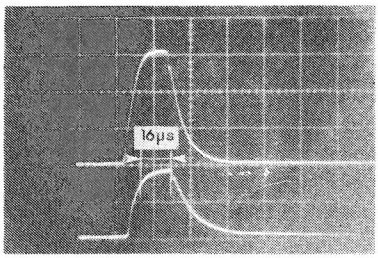

Figure 2 - Beam current (upper trace, 200 mA/cm) and discharge current (lower trace, 5 A/cm) under conditions of case 2. Time scale is 20 µs/cm.