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ABSTRACT

The production of toxic gases is one of the safety problems arising from the use of electron accelerators. The most important of these gases are ozone and nitric oxides. Regarding the first, there is a fair amount of experimental data available, even though this data is not completely conclusive. For the second, there is a real lack of experimental information.

With the aim of gathering data which could be directly helpful for protectionistic evaluations, it was deemed useful to study the formation of the above mentioned toxic gases in the air contained in a unventilated system exposed to the radiation beam of a linear accelerator.

The results of these measurements have been interpreted establishing simple relationships between the concentrations measured and the rate of energy deposited per unit of volume of irradiated air.

1. - INTRODUCTION

It has been long known that ionizing particles induce the formation of numerous toxic gases (O_3, NO, NO_2, NO_3, N_2O, N_2O_3, N_2O_4, N_2O_5, HNO_2, HNO_3) in the air. Apart from ozone, for which there is a fair amount of data available, the experimental knowledge is rather scarce.

The production processes of the above mentioned toxic gases do not have any threshold energy value except that of the excitation and ionization processes, which is anyway very modest. The most dangerous of these is certainly ozone, an unstable gas that decomposes slowly at room temperature producing a variety of compounds including O_2, N_2, N_2O_5 and HNO_3. The decomposition time depends greatly on the geometry and the nature of the materials present.

The nitric oxides NO and NO_2, generally named NO_x, are also formed under the action of ionizing radiation. The NO is transformed by the O_3 in NO_2, which is therefore the predominant nitric oxide.

The formation of these gases is characterized by the value of the parameter "G", which represents the number of molecules produced for each eV of energy absorbed in the system under consideration.

Table I summarizes some of the informations about the toxic gases under discussion.

TABLE I - TLV and G values for toxic gases (data from IAEA 79).

G A S	TVL (ppm)	G (molecules per eV)	
		Low dose rate(*)	High dose rate(*)
Ozone O_3	0.1	0.074	0.103
Nitric ozone NO	25		
Nitrogen dioxide NO_2	5	(0.048)	(0.0015)

(*) High dose rate means instantaneous dose rate (during beam pulse) greater than about 3.10^{24} eV . g^{-1} . s^{-1} to air. Theoretical values are in parenthesis.

The TVL (Threshold Values Limits) reported in Table I are intended for 8 hours per day continuous exposure for a total of 40 hours per week.

Considering the lower TVL, the high radiolytic yield and the chemical reactivity, ozone is almost always the limiting compound among those listed above.

The ease with which ozone decomposes makes it also an effective oxidizing agent especially in the presence of dampness. The oxiding reaction takes places in most metals. Stainless steel and aluminium resist its action rather well. Plastics and certain elastomers are degraded.

Recurring articles have appeared in the literature in which there is talk of studies on ozone production in the air by ionizing radiation, both around important irradiators of Co-60 (ex. Le64, Ke63, Ni82) and around electron accelerators (ex. Lo62, La65, Ge65, Br71, Ne75, Ca79, Sw80, Ho80, Fa82). The formation of other compounds, such as NO (Lo62) and HNO_3 (Lo62, Ne75), has also been considered but only in very rare cases.

The formation of toxic gases in the air can be a particular problem of some importance near synchrotron radiation machines. This subject has been accurately studied as part of the project developed for one of these machine, the LEP, the large storage ring under construction at CERN (Fa82, Fa84).

It is worthwhile remembering that the formation of toxic gases is generally treated in all the technical guidebooks dedicated to protective measures around electron accelerators (for ex. NBS64, NCRP77, IAEA79).

Therefore, taking measurements of the concentration of ozone (O_3) and of nitric oxides (NO_X) formed in the air by the electron beam of Frascati National Laboratories linear accelerator was thought to be useful. The results obtained are shown in this paper.

2. - FORMATION AND DECOMPOSITION OF O_3 and NO_X

As already stated, ozone is the better studied induced toxic gas. In order to describe its formation by air ionization and its decomposition by chemical reaction or by irradiation in a closed system (that is, one without ventilation), the following differential equation can be used:

$$dN/dt = IG - \alpha N - kIN \qquad (1)$$

where dN/dt is the rate of formation or decomposition of ozone ($cm^{-3}s^{-1}$), I the power deposited in air per volume unit ($eV\ cm^{-3}s^{-1}$); G the number of molecules formed per eV (eV^{-1}); α the decomposition constant (s^{-1}); N the concentration at time t (cm^{-3}); k a constant describing the destruction by the action of radiation ($eV^{-1}\ cm^{-3}$).

The integration of Eq. 1 gives:

$$N(t) = \frac{IG}{\alpha+kI}\left[1-e^{-(\alpha+kI)t}\right] \qquad (2)$$

From eq. 2 it can be seen that the concentration of ozone tends to reach an asymptotic saturation value N_{sat} expressed by:

$$N_{sat} = \frac{IG}{\alpha+kI} \qquad (3)$$

Some numerical values of G are indicated in Table I. For α the values reported in the literature vary greatly because of environmental conditions and in particular temperature, dampness and the surfaces present. Evaluations of k are very rare. In the above mentioned LEP project a value of $2.3.10^{-4}\ s^{-1}$ was used for α and $1.4.10^{-16}\ cm^3\ eV^{-1}$ for k (Fa84).

As for the formation of NO_x by irradiation, no analytic treatment has ever appeared in the literature. In this paper it is assumed that as a first approximation an equation similar to eq. 1 can be written for them as well. Since the compounds involved are however quite stable it will be $\alpha \simeq 0$. Given this, the concentration of the gas under discussion should increase linearly to the irradiation time until $kIt << 1$.

3. - MEASUREMENT RESULTS

These measurements concern the production of O_3 and NO_x by irradiation of the air contained in a closed system exposed to the radiation fields produced by the 40 kW linear accelerator at the Frascati National Laboratories.

A DASIBI model 1003AH analyzer was used to measure the ozone concentrations and a Beckman model 952A was used for the nitric oxides. The DASIBI analyzer determines the ozone concentration in an air sample by means of the ultraviolet radiation absorbed by the ozone molecules. The Beckman nitric oxide analyzer uses chemiluminescent detection.

The variability of the environmental conditions influence both the reactions of the formation and decomposition of the gases and to a great extent even the response of the analyzers.

A first set of measurements were taken by exposing the air sample to be examined directly to a beam of accelerated electrons at various average currents.

The choice of the electron energy depended upon the working conditions of the accelerator since, within the limits of the energies used (150-300 MeV), this has very little influence on the concentration of the gases produced (Ca79).

The concentration in ppm of ozone and of nitric oxides, measured exposing the air in an 18.5 liter container directly to an 850 nA electron beam accelerated at 230 MeV are shown, as an example, in Fig. 1 and 2 respectively.

The results presented seem to confirm the above mentioned considerations. The tendency for ozone concentration to reach a saturation value after 1-2 hours of exposure to the beam can be observed. The saturation value depends, of course, on all the parameters involved (air volume, beam current, etc.).

For the nitric oxides, at least for the irradiation times considered here, a linear

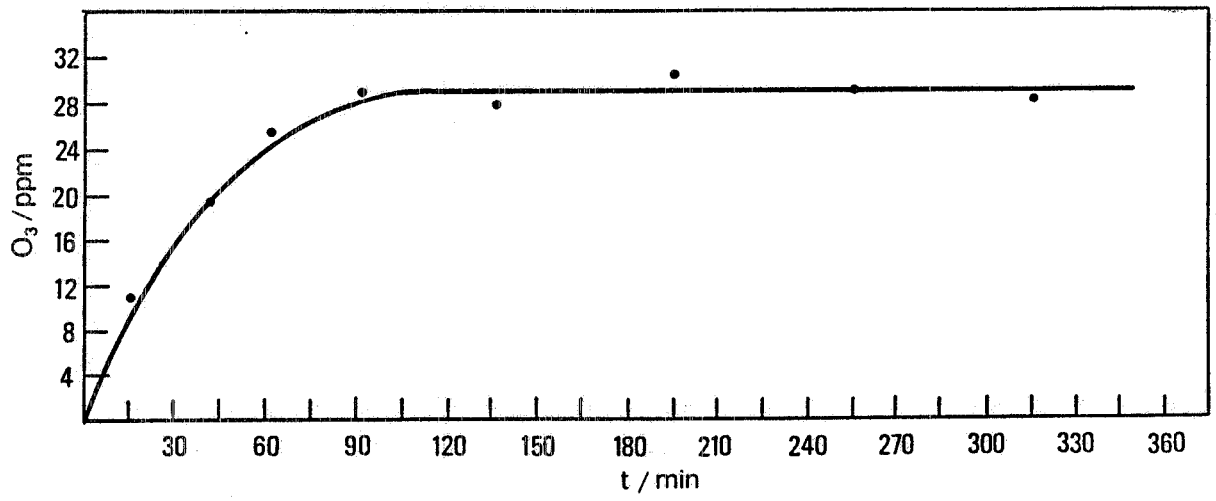

FIG. 1 - O_3 concentration in air measured in a closed 18.5 liter container as a function of irradiation time (E=230 MeV; i=850 nA; $I=9.9.10^{15}$ $eV \cdot cm^{-3} \cdot s^{-1}$).

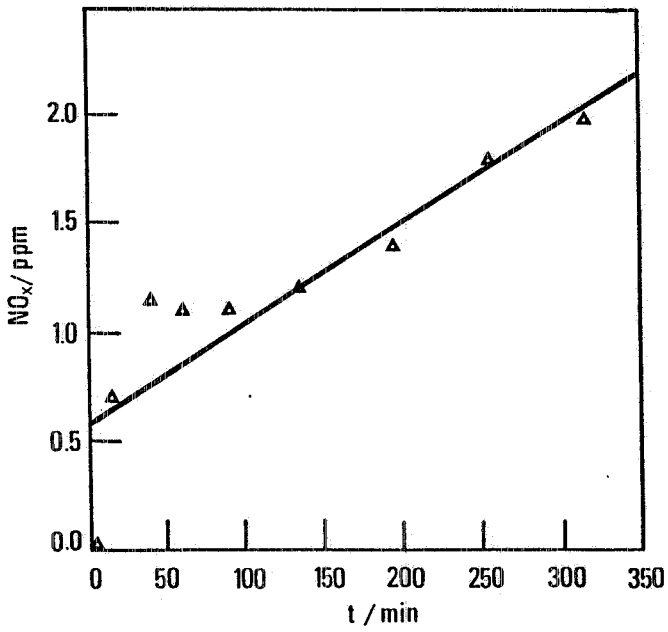

FIG. 2 - NO_x concentration in air measured in a closed 18.5 liter container as a function of irradiation time (E=230 MeV; i=850 nA; $I=9.9.10^{15}$ $eV \cdot cm^{-3} \cdot s^{-1}$).

increase over time can be observed. This would seem to confirm the validity, in this case too, of the eq. 1, where however the chemical decomposition constant α is equal zero.

The linac electron beam permitted the use of very high values of energy deposited per volume unit. However, because of the modest size of the beam, the sample analysed had a larger volume than that actually hit. On the other hand, because of the limitations imposed by the analyzer's flux, the exposure of very small volumes was not acceptable.

In order to compare the results of these measurements with those of uniform irradiation of the total volume, it is therefore necessary to account for the dilution of gases produced by scaling down the concentrations measured.

It must be considered however that this procedure could lead to systematic errors, which are difficult to evaluate, since the condition of dynamic equilibrium of the gases produced could be different from that reached in a volume completely irradiated. In other words, it is possible that the value of the saturation concentration determined in this way would not be precise enough.

Another cause of scarce accuracy could be due to the large fluctuations of the intensity of the electron beam current.

To try to overcome the first problem, a second set of measurements were made exposing volumes of air to the electromagnetic radiation produced in the direction of 90° to the electron beam incident on a thick lead target. The volume analyzed was, in this manner, completed exposed to ionizing radiation even though not totally uniformly.

The energy rate deposited per unit of volume, determined by dose measurements made using thermoluminescent dosimeters (Harshaw TLD700), was in fact different from point to point. In examining the results, the average value was used.

It is worth observing that the energy deposited per unit of volume in this second set of measurements was much smaller than in the previous set.

Some results are shown, as examples, in Fig. 3 and 4 for O_3 and NO_x respectively.

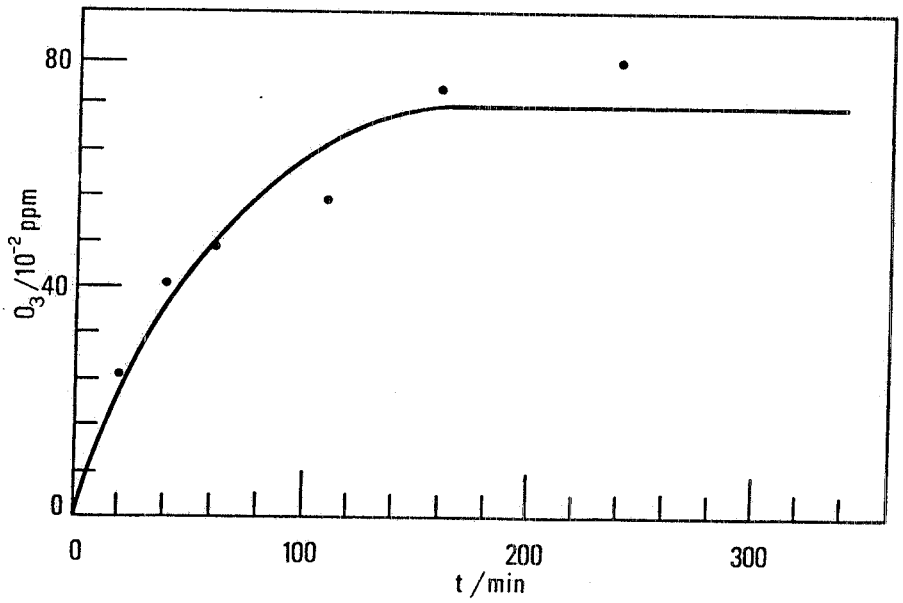

FIG. 3 - O_3 concentration in air measured in a closed 25 liter container exposed to radiation field produced at 90° by a 300 MeV, 480 nA electron beam incident on a thick lead target as a function of irradiation time ($I=4.1.10^{11}$ eV $\cdot cm^{-3} \cdot s^{-1}$).

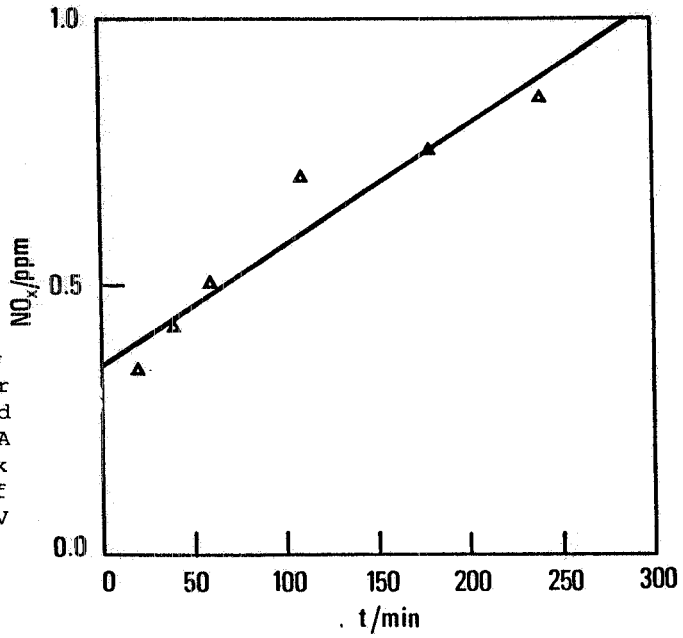

FIG. 4 - NO_X concentration in air measured in a closed 25 liter container exposed to radiation field produced at 90° by a 300 MeV, 480 nA electron beam incident on a thick lead target as a function of irradiation time ($I=4.1.10^{11}$ eV $\cdot cm^{-3} \cdot s^{-1}$).

As can be seen, for equal irradiation times, the ozone concentration is 10 to 20 times greater than that of the nitric oxides when the sample is exposed to the electron beam, but on average comparable when the sample is exposed to the radiation produced in the lead target. This fact seems to be qualitatively justified by the different values of G ratios of the ozone to the nitric oxides in the case of high or low dose rate exposures.

The concentration of ozone at saturation and that of the nitric oxides reached after a preset exposure time against the rate of energy deposited per unit of volume were also studied. In doing this the above discussed corrections for taking into account the differences between the volume irradiated and volume of the air sample under study were applied to the first set of measurements.

Figs. 5 and 6 show the results for ozone and for the NO_X respectively. For the latter, the results of the measurements taken after 5 hours of irradiation were considered.

The experimental points were interpolated with polynominal fits variance. Specifically for the ozone curve is $\sigma^2 = 6.3.10^{-2}$, and for the NO_X curve is $\sigma^2 = 7.0.10^{-2}$.

Fig. 5 shows a satisfactory qualitative agreement with the prediction of Eq. 3. In fact for the lower values of I the curve is approximately linear, while increasing I it tends to an asymptotic value. The first portion of the curve can be well represented by $N_{sat} \propto I^{0.8}$ (dotted line in figure), as previously proposed (Ca79).

With the aim of evaluating the saturation concentration of the radio-induced ozone from a strictly protectionistic point of view, it must moreover be observed that the entire curve of Fig. 5 can also well be described by the simple linear relationship between N_{sat} and I ($N_{sat} = 40I + 2.10^{11}$).

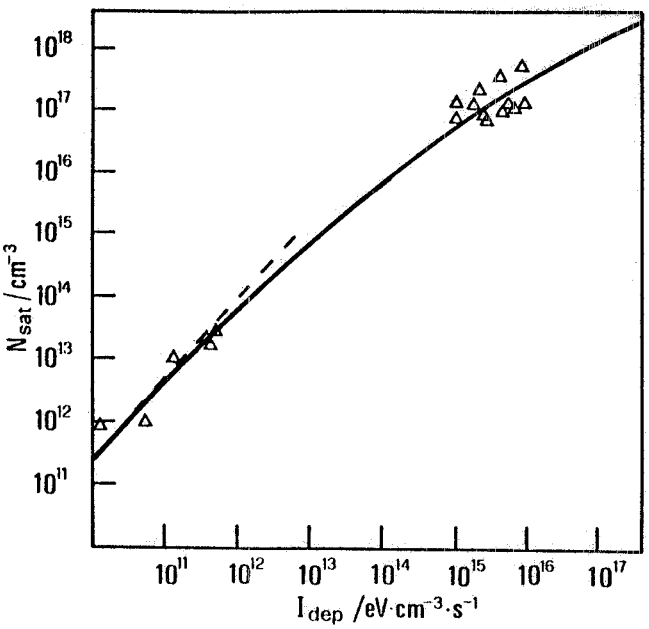

FIG. 5 - O_3 concentration at saturation as a function of the rate of energy deposited per unit of volume of irradiated air.

As far as the nitric oxides are concerned, based on Fig. 6, their concentration after 5 hours of irradiation seems to follow a $I^{0.6}$ dependence.

The numerical values of the various parameters (G, α, k) that govern the formation and the decomposition of the compounds being studied could be derived from the curves in Figs. 5 and 6. However, experimental uncertainties above discussed, make this a difficult task. It is therefore preferable to consider the results of these measurements simply as suitable for establishing the orders of magnitude of the concentrations involved and the empiric relationships between these concentrations and the energy rate deposited per unit of volume of irradiated air.

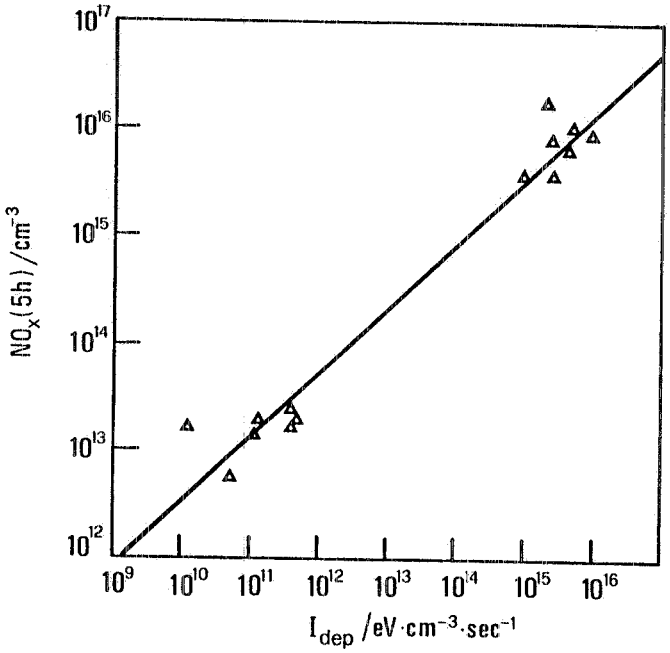

FIG. 6 - NO_x concentration after 300 minute of irradiation as a function of the rate of energy deposited per unit volume of irradiated air.

4. - CONCLUSIONS

A response, useful for protectionistic purposes, about the relationships between the concentration of ozone and nitric oxides and the energy rate per unit of volume deposited in the air by the ionizing radiations was obtained and a qualitative confirmation of the calculation models proposed was found. The results of the measurements were also interpreted in terms of empirical relationships for simple practical use.

Specifically, as far as ozone is concerned, it is suggested that, as a first approximation, a simple law of linearity between saturation concentration and the energy rate deposited per unit of volume can be used at least in the range of values explored in this experiment.

For the nitric oxides the concentration after 5 hours of irradiation seems to depend upon the rate of energy deposited per unit of volume according to a power law with an exponent of 0.6.

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