

Behaviour of NO_x in air-fed ozonizers

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Abstract - The influence of humidity, gas pressure, power density, and cooling temperature on the NO_x formation have been investigated. The experimental results are compared with calculations based on a rate equation system of 75 chemical reactions and a considerably reduced system. The importance of the different nitrogen oxides in ozonizers is discussed. While the N₂O concentration does not influence the ozone generation, the N₂O₅ ↔ NO₂ + NO₃ equilibrium affects its formation via catalytic processes.

INTRODUCTION

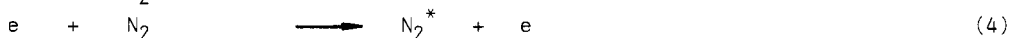
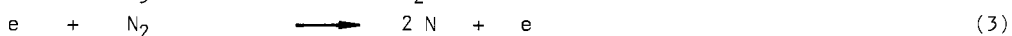
Recently new fields of application of ozone have been under consideration where large amounts are needed. That is why the efficiency of its production becomes more and more important. Air-fed ozonizers have only about half the efficiency of oxygen-fed devices. This reduction results from two effects. First, the electrical energy within the discharge of ozonizers is fed besides in oxygen in nitrogen, too, dissociating and exciting nitrogen molecules. Secondly, the presence of small amounts of nitrogen oxides reduces the yield of ozone.

The interaction of the discharge with nitrogen cannot be avoided. But there is a chance to affect the nitrogen oxides in order to improve ozone generation.

NO_x FORMATION

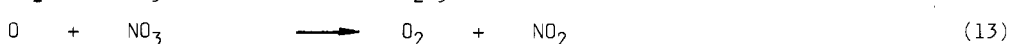
In the gas discharge phase of the ozone generation process reactive oxygen and nitrogen atoms as well as excited molecules are produced within several nanoseconds (ref. 1). These particles react within microseconds to give NO, NO₂, NO₃, N₂O, N₂O₅, and O₃.

In order to describe the NO_x formation in ozonizers theoretically we use a rate equation system including four electron impact processes (M: collision partner):



(N₂^{*}: electrically excited molecule (ref. 2))

and 75 reactions between the neutral gas particles. In the normal range of operation the most important of these reactions are:





If traces of water (or hydro carbons) are present HNO_3 is produced additionally:



The concentrations of the different species are calculated by solving the rate equations numerically (ref. 3). The rate coefficients of the reactions 5 to 19 are functions of the gas temperature. The temperature distribution within the discharge gap is calculated solving the heat conduction equation.

Figure 1 shows a typical example of measured concentrations of O_3 , N_2O , and N_2O_5 over the energy density P/Q compared with calculated concentrations. In this case the power P has been taken constant, and the gas flow rate Q has been changed in order to get different energy densities.

As long as a large surplus of ozone molecules is present and at low gas temperatures the equilibrium of reaction (12) is shifted nearly completely towards N_2O_5 . In this case N_2O_5 , N_2O , and possibly HNO_3 molecules are only detected.

The N_2O and N_2O_5 concentrations rise linearly with the energy density. This is in agreement with the fact that the production rate of nitrogen atoms (reaction 3) and excited molecules (reaction 4) are independent of the energy density and that all nitrogen atoms are converted to N_2O_5 as long as ozone is present.

The ozone concentration passes through a maximum. In the rising range of its concentration the production of oxygen atoms (reaction 1 and 18) and thereby of ozone is nearly proportional to the energy density. In this region the efficiency of the ozonizer has its highest values. - With rising ozone concentrations the ozone destroying processes (reactions 2, 6, and 8) become more and more important leading to a reduced increase of its concentration. Besides, with rising NO_x concentrations even the low densities of nitrogen oxides like NO , NO_2 , and NO_3 are not any longer negligible with respect to catalytic process chains like (ref. 4)



and



At higher energy densities the catalytic processes may destroy the ozone concentration totally.

The concentration of N_2O and N_2O_5 is about one percent of that of ozone in the operation range of ozonizers.

EXPERIMENTAL RESULTS

In order to find out NO_x and O_3 dependencies some operating conditions are varied i.e. humidity and pressure of the process gas as well as power density and cooling water temperature. The geometrical dimensions are unchanged.

The experiments are performed with a single tube ozonizer with a discharge area of about $.1 \text{ m}^2$. The gap distance is 1.3 mm. The earthed tube is water cooled. The ozonizer is supplied by a 2000 cycles per second power source. - The nitrogen oxide concentrations are measured by IR-spectroscopy (ref. 5), the ozone concentration by UV-absorption techniques.

Humidity

The humidity of the process gas was varied between $< 10 \text{ ppm}$ ($\Delta < -60^\circ \text{C}$) and $900 \text{ ppm H}_2\text{O}$ ($\Delta -20^\circ \text{C}$ dew point). Even with very dry air a background of HNO_3 has been detected linearly rising with energy density. At high moisture contents N_2O_5 is not detectable. N_2O_5 reacts with H_2O according to reaction (19).

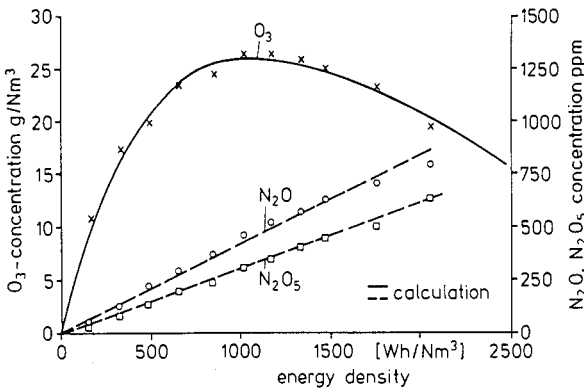


Fig. 1. Particle concentrations in an ozonizer (< 10 ppm H₂O, 1.2 bar, 3.8 kW/m², cooling temperature T_c = 10⁰ C)

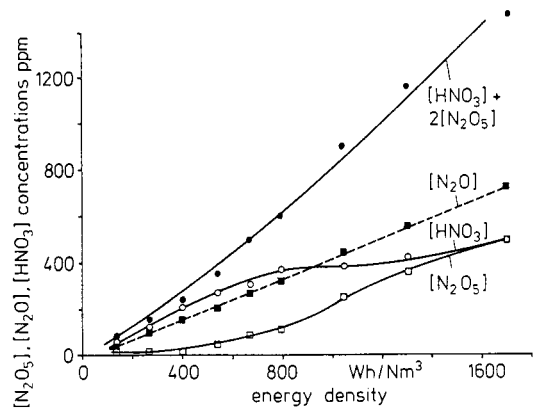


Fig. 2. Nitrogen oxides concentrations at 100 ppm H₂O (1.2 bar, 3.8 kW/m², T_c = 10⁰ C)

In Fig. 2 the development of HNO₃, N₂O₅, and N₂O concentrations is shown for 100 ppm H₂O. - As long as H₂O is present the N₂O₅ concentration is zero while the HNO₃ component rises. When all H₂O molecules are converted to HNO₃ the N₂O₅ fraction increases. The sum of all measured nitrogen oxides (NO_x = 2 N₂O₅ + HNO₃) increases more than proportional with energy density when all H₂O molecules are decomposed.

Further experiments show that the NO_x production does not change with rising moisture content while the N₂O production decreases slowly with increasing humidity.

An interesting phenomenon has been observed in connection with the humidity influence. The H₂O molecules destroy the N₂O₅ particles via reaction (19). This means that there is a further reduction in the traces of NO, NO₂, and NO₃. Because of this the catalytic chains are less important in the presence of humidity (Fig. 3).

Pressure

The pressure has nearly no influence on the N₂O yield in the investigated pressure range from 1.2 to 2.5 bar while the N₂O₅ yield rises slowly with pressure. - Figure 4 shows the related N₂O₅ content over the ozone concentration. An interesting fact is that the poisoning of the ozonizer due to catalytic processes is smaller at higher pressures and equal ozone concentration.

Power density

In the range of the investigated power densities of 1.5 kW/m² to 5 kW/m² the nitrogen oxide concentrations do not vary with power density at fixed energy densities. This is in agreement with the facts that (i) the production rates of nitrogen atoms and excited molecules remain constant with power density and (ii) nearly all produced nitrogen atoms are finally oxidized to N₂O₅ respective a fixed portion of the excited nitrogen molecules are converted to N₂O.

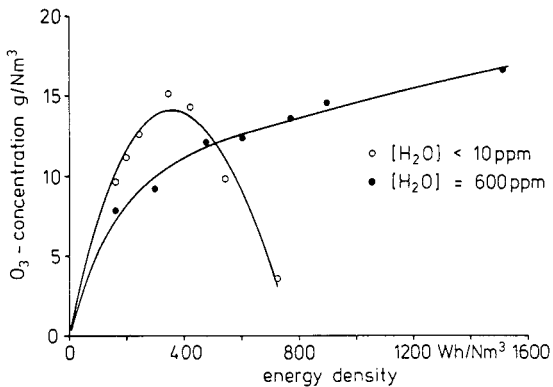


Fig. 3. Ozone concentration at < 10 and 600 ppm H₂O (1.2 bar, 3.8 kW/m², T_c = 10⁰ C)

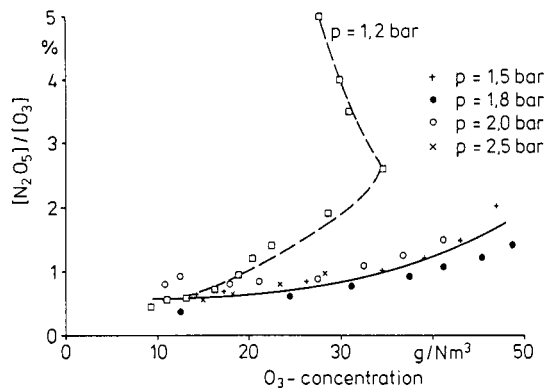


Fig. 4. Related nitrogen pentoxide concentration at different pressures (< 10 ppm H₂O, 3.8 kW/m², T_c = 10⁰ C)

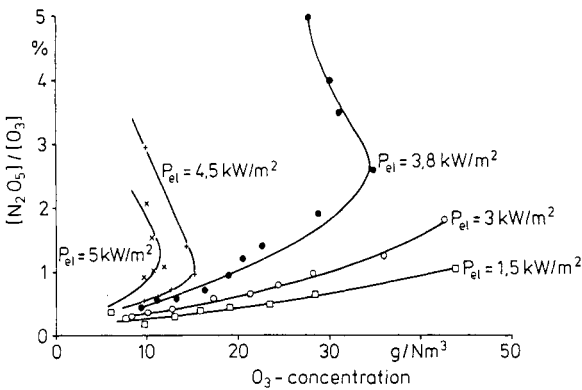


Fig. 5. Related nitrogen pentoxide concentration at different power densities (< 10 ppm H_2O , 1.2 bar, $T_c = 10^\circ C$)

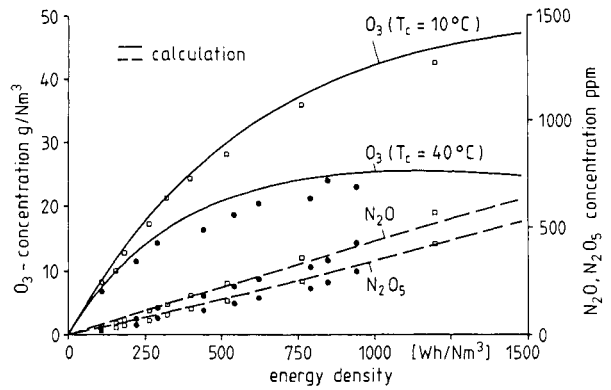


Fig. 6. Ozone concentration at different cooling water temperatures (< 10 ppm H_2O , 1.2 bar, $3.8 kW/m^2$)

Figure 5 describes e.g. the N_2O_5/O_3 ratio over the ozone concentration. At constant ozone concentration the nitrogen oxide contents rise with power density. The maximum attainable ozone concentration depends dramatically on power density.

Cooling water temperature

Varying the cooling water temperature has a similar effect. An increase of the temperature does not influence the N_2O and N_2O_5 generation efficiency but reduces the ozone production (Fig. 6). Therefore the N_2O_5/O_3 ratio is increasing with raised cooling water temperature (Fig. 7).

DISCUSSION

The influence of humidity on the ozone and nitrogen oxide formation is quite different. The most obvious effect is the variation in the composition of the different nitrogen oxide species. At low H_2O concentrations (< 10 ppm) N_2O_x and N_2O can be detected only. With rising humidity N_2O_5 is converted and essential concentrations of HNO_3 appear (reaction 19). At high H_2O concentrations (> 300 ppm) HNO_3 and N_2O are observable only. While the composition of the nitrogen oxides varies strongly with moisture contents the NO_x production rate ($NO_x \equiv 2 N_2O_5 + HNO_3$) remains nearly constant. This effect can be explained assuming that the nitrogen atom production via the electron collision reaction (3) is not essentially affected by humidity.

The N_2O production rate on the other hand is reduced with increasing humidity (about 25% at 800 ppm H_2O and $p = 1.2$ bar). Because N_2O is mainly formed via reactions (4) and (17) this means a diminution of excited nitrogen molecules at increased moisture content.

In the normal range of operation the ozone generation efficiency is influenced by humidity. Commercial ozonizers operate with extremely dry air (< 10 ppm H_2O). Though larger moisture contents reduce the poisoning effect (Fig. 3) the reduction of the ozone concentration is much more important leading to a diminished ozone yield.

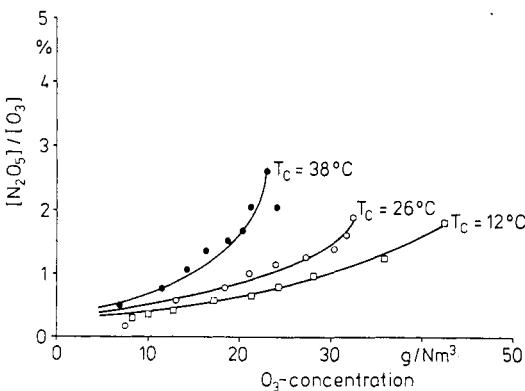


Fig. 7. Related nitrogen pentoxide concentration at different cooling water temperatures (< 10 ppm H_2O , 1.2 bar, $3 kW/m^2$)

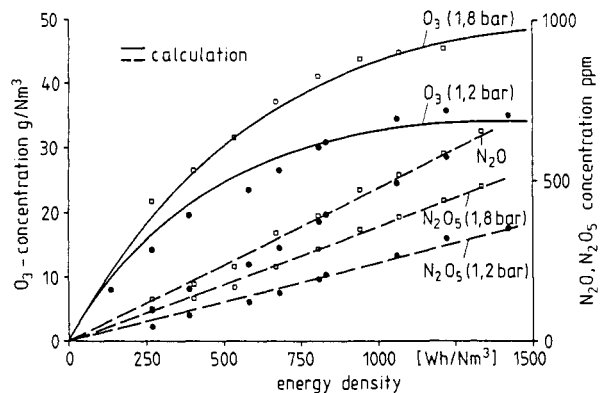


Fig. 8. Ozone and nitrogen oxide concentrations at different pressures (< 10 ppm H_2O , $3.8 kW/m^2$, $T_c = 10^\circ C$)

Increasing the gas pressure leads to a higher ozone generation efficiency (Fig. 8). There are two reasons for this behaviour. The equilibrium in reaction (12) will be shifted towards N₂O₅ so that the traces of NO₂ and NO₃ are further reduced and the catalytic reaction chains (reactions 10, 9, 16, 13, and 14) are less important. The ozone production via the three body collision reaction (5) is also favoured at increased pressure.

The N₂O yield is not influenced by pressure while the N₂O₅ yield rises with pressure. The calculated NO_x concentrations in Fig. 8 are gained adapting the reaction constant of equation (3) to the measured N₂O₅ values respective fitting a reduced reaction equation system to measured N₂O values (ref. 2). From this follows a pressure dependency of the reaction rate constant of reaction (3). The reason is not yet understood.

The influence of power density on the ozone and nitrogen oxide generation is shown in Fig. 9. The formation of the nitrogen oxides is not affected by power density, however the ozone production is remarkable reduced. This can be explained with elevated temperatures in the process gas at rising power densities.

The reaction kinetics within the ozonizer are determined by temperature. Power density as well as cooling water temperature influence the distribution of the temperature within the discharge gap. Solving the heat conduction equation a mean value of "reaction temperature" T_R can be evaluated:

$$T_R = T_C + a P_{el}$$

(P_{el} = power density; a = const., depending on geometry)

Introducing the reaction temperature T_R the influence of power density and cooling water temperature on the nitrogen oxide and ozone formation is combined.

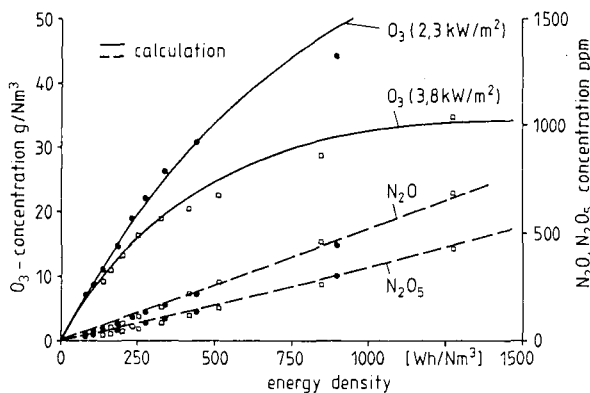


Fig. 9. Ozone and nitrogen oxide concentrations at different power densities (< 10 ppm H₂O, 3.8 kW/m², $T_C = 10^\circ$ C)

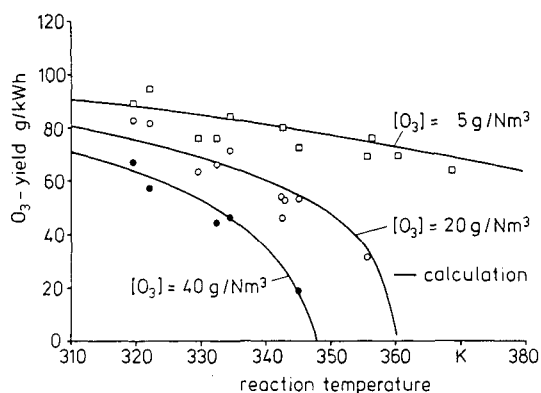


Fig. 10. Ozone yield at different ozone concentrations (< 10 ppm H₂O, 1.2 bar)

While the nitrogen oxide generation efficiency is practically independent of the reaction temperature the ozone yield decreases with rising reaction temperature due to a reduced ozone production via reaction (5). Additionally, the ozone destroying catalytic processes accelerate with increasing reaction temperature. Both processes lower the ozone yield. This effect is more distinct at high ozone concentrations (Fig. 10).

CONCLUSION

The calculated concentration values based on a reduced system of reaction equations presented in this paper are in rather good agreement with measured values. Therefore the reaction mechanisms within air-fed ozonizers can be interpreted by this system.

Remarkable concentrations of N₂O, N₂O₅ and in the presence of humidity HNO₃ are detected within the normal range of operation of ozonizers. Varying pressure, power density, and cooling water temperature there are only weak dependencies on the N₂O yield. N₂O is chemical inert for the ozone generating process and of less importance.

N_2O_5 is much more important. It is in a chemical equilibrium with lower nitrogen oxides and in case of humidity with HNO_3 . The lower nitrogen oxides reduce the ozone concentration via fast catalytic processes. - Lowering the reaction temperature and rising the pressure shift the equilibria towards N_2O_5 and thereby enlarge the ozone yield.

Acknowledgement

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