OZONE FOR NOx ELIMINATION FROM WASTE GASES

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Abstract

Nitrogen oxides in this day take a major place as one of the most hazardous pollutants of atmosphere. Some chemical properties of nitrogen oxides evoke a number of methods prohibiting their emission and the thermodynamic analysis of their production indicates the variants of the processing design which would allow to restrict the undesired synthesis. Oxidation of NO by means of oxygen is a very slow reaction. Therefore the application of a strong oxidizer becomes very important. The use of ozone appears to be very attractive from the view point of technological processes.

Introduction

Application of plasma to the protection of natural environment is becoming a more and more widely and frequently discussed subject at scientific symposia concerning plasma chemistry as well as the environment. It is mostly direct application of plasma that is discussed but it is worth pointing out that plasma can be also efficiently applied in an indirect way. One can talk about effective application of plasma to the environment protection when the application of plasma technology yields positive economic results in activities on economic and civilisation grounds. From this point of view using ozone for to control emission of nitrogen oxides in industrial flue gases can be considered to be one of the most important indirect applications of plasma chemical methods. Reasoning the same way one can find that surface treatment that diminishes grind ability and extends life of a device or tool can viewed as an environmental technique. Ozone applications make even a better example of such a technique as in each case of the production of this strong oxidiser is on the spot and productivity and technological parameters have to meet strictly the requirements of the process that applies the generated ozone. The simplest example is classical ozone application to water treatment where the pressure of working gas in an ozonizer has to take into account flow resistance and barbotage through the treated water. The course of processes applying ozone should be also considered in a feedback way so as the design of an ozone generating installation was adapted to the needs. The presented paper shows an example of an ozone synthesis system coupled with the proposed technological process for removing nitrogen oxides from flue gases.

Experimental Procedure

An installation was constructed for to realize research into the course of nitrogen oxides removal from industrial flue gases by means of ozone. The installation was composed of two essentially different blocks. The first one was an ozone generating apparatus and the other one consisted of a series of devices in sequence through which nitrogen oxides flew. At a determined place of the sequence ozone was supplied from the first setup. A diagram of the installation is shown in the Fig.1. Ozone was generated in an ozonizer with a thin-layer dielectric supplied from a HV transformer. A diagram of the ozonizer is presented in the Fig.2. The following systems could be distinguished in the ozonizer: electrical energy supply system, electrical measurement system, gas preparation system, cooling system, and control-measurement system. Transformer and auto transformer ensured smooth control in the range of 0-17 kV.

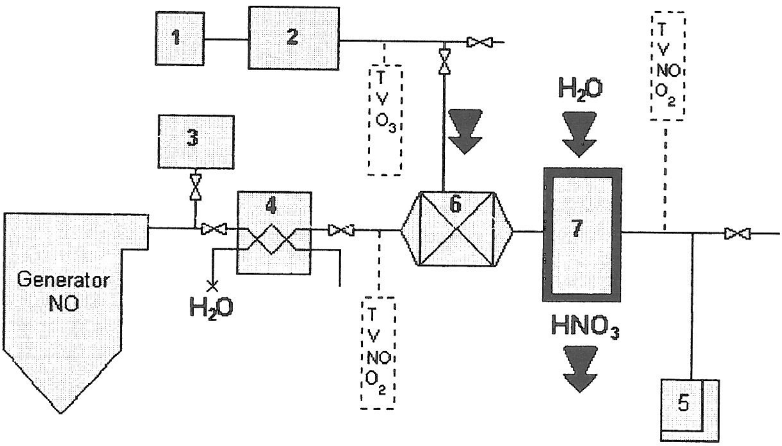


Fig 1. NOx removal installation scheme by the oxidation-absorption process.

Overcurrent relay protected the setup against damage in case of dielectric breakdown. Substrate gas passed subsequently through drying columns with calcium chloride, soda lime, silica gel , then through rotameter, and only then it was supplied to the ozonizer. The concentration of obtained ozone could be controlled within a wide range by the control of voltage and substrate gas flow. Measurement of ozone concentration in post-reaction gas was performed by means of Anseros meter Ozomat GM.
Nitrogen oxides were obtained in a separate generator from a reaction of nitric acid and potassium nitrite according to the oxidation-reduction equation, then were diluted in a nitrogen flux and transferred to a mixer where the oxidation reaction of NO with ozone took place. Kinetics of the process was analysed separately and showed that NO to NO_2 oxidation reaction by means of ozone in stoichiometric quantities was a very

quick process at rate constant of k_2 =10800 $m^3/mole^2sec$ [2,7]. Kinetic equation describing the dependence of the removed quantity of NO_x on the duration of the reaction with ozone at stoichiometric concentration of reactants was derived. A similar equation to compare oxidation rate when oxygen was applied as an oxidizing agent was also derived (however, oxidation of NO by means of oxygen is a slow reaction, where constant rate of the third order reaction is k_1= 0.01325 m^6/ mol^2sec [1]). On the basis of those equations rates of the processes could be determined and efficiency of NO removal by means of O_2 and O_3 could be evaluated. It follows from the form of the kinetic equations that the time needed for removal of the same quantity (x) of NO in both reactions should be compared. Hence, it is the ratio of time needed to remove the same quantity of NO in each reaction that can be a relative measure of the process rate in both reactions. Time periods needed for the removal of 90% of NO in a two-stage process of NO oxidation by means of oxygen and ozone - the first stage with only oxygen used and the other one when both oxygen and ozone acted as oxidizing agents - were compared. Test calculations were performed for technological conditions of flue gases emission depending on emission sources taking values in the range of 500ppm-5600ppm. Another assumption was that the final content of NO was not greater than 50ppm=0.00223 mole/m^3. It was also assumed that the duration of the first stage of the process i.e. oxidation of NO by means of oxygen from air (concentration: 9 mole/m^3) was determined by the reactor's volume and gas flow rate (the duration was t = 500s) . Initial concentration of ozone was equal to respective initial concentrations of NO in the second stage of the process. Time needed for the removal of NO to the 50ppm concentration in dependence on initial NO concentration in flue gas is presented in the Table 1.

c NO [mole/m^3]	(x)NO Removal stage I [mole/m^3]	c O_3 [mole/m^3]	(x)NO Removal stage II [mole/m^3]	Time stage II [sec]
0.0223	0.0133	0.0090	0.0868	3.1 E-3
0.0445	0.0320	0.0125	0.0103	7.4 E-3
0.0890	0.0750	0.0140	0.0118	3.4 E-2
0.1115	0.0970	0.0145	0.0123	3.5 E-2
0.2230	0.2070	0.0150	0.0136	3.6 E-2
0.2500	0.2340	0.0160	0.0138	3.6 E-2

Table 1. I stage - oxidation by means of oxygen from air; II stage - ozone additive; In all cases final NO concentration was 50ppm.

The performed experiments have shown that theoretically possible stage of NO oxidation to NO_2 and to N_2O_5 is a very slow process and it is impossible in practice to oxidize nitrogen monoxide (NO) to N_2O_5 for to obtain nitric acid. Further oxidation proceeds in liquid phase.
Steam in the oxidation process in its gas phase accelerates the process and increases the efficiency of nitric acid during the very absorption process. The main aim of the

research was to trace the course of oxidation and absorption processes in the presented installation at various initial concentrations of NO and ozone and various contact times. Experimental results are presented in the Fig. 3 and Fig. 4. On the basis of the obtained results and the following equation mass exchange coefficient can be determined by

$$k = \Delta n / F \, \Delta \Pi$$

where: F is the contact surface of two phases (sprayed area), Δn - mass flow of absorbed nitrogen oxide [mole/sec E -6], and $\Delta \Pi$ is the driving module of the process [mole/m^3]. The efficiency of the action of ozone was determined by calculating a ratio of k_T coefficient obtained for given conditions with an oxidizing agent containing ozone additive to k_{T0} coefficient obtained for the same conditions but with oxygen only used for the oxidation process. Results of the calculations are presented in the Fig. 5. The remaining data show that when ozone is applied it is possible to obtain even 90% decrease of NO concentration. The calculated mass exchange coefficient grows by over two times even at substoichiometric ratio of ozone to nitrogen monoxide. The obtained data make possible to calculate the efficiency of an ozonizer that should be installed in the device since it is possible to calculate the necessary quantity of ozone and contact time of gas mixture containing ozone with gas flux containing nitrogen oxides. At given nitrogen oxide concentration in flue gas and its flow rate known the to-be-obtained parameter is the degree of NO removal from gas phase.

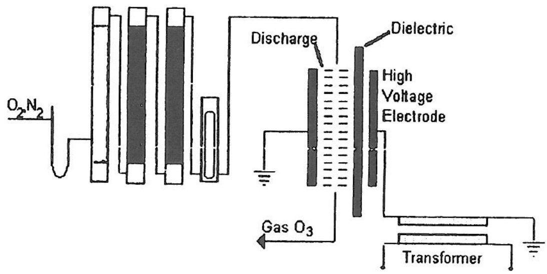


Fig 2. Ozone production scheme.

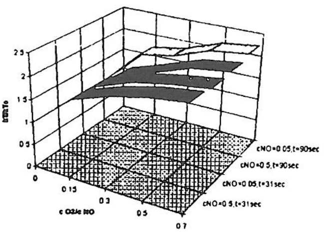


Fig 5. Relation k_T/k_{T0} versus concetration of O_3 /concentration of NO

Discussion

The presented research work concerned investigation into the intensification of absorption of nitrogen oxides from diluted flue gases in water under the influence of ozone introduced to the gas phase as an oxidizing agent.

Physical processes and chemical reactions characteristic for mass exchange in gases involved in that process are very complex and quantitative description of nitrogen oxides absorption is very difficult. Mass transport from one phase to the other can be described numerically through the application of laws concerning diffusion processes but the mechanism of the exchange is not much explained although there is a number of research works devoted to the question [4,6].

There are several factors that make the absorption process so complex as simultaneously proceeding oxidation of nitrogen oxide or diffusion of the forming nitrogen oxide on its way between the reaction site and the gas core [8,9].

In the presence of oxygen and ozone the absorption process in counter-current conditions includes the following set s of physical and chemical reactions:

a) oxidation of NO to dioxide or even higher oxides,
b) interaction among nitrogen oxides of various oxidation degree,
c) interaction between nitrogen oxide and steam resulting in the occurrence of *mist* or *steam* of nitric and nitrous acids,
d) diffusion and possibly convection processes in the gas phase,
e) processes at the verge of the phases including absorption as well as desorption phenomena,
f) diffusion phenomena,
g) chemical reactions in the liquid phase.

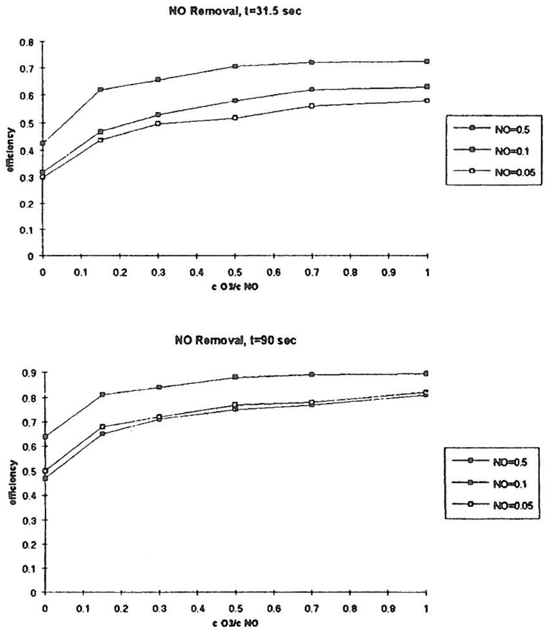


Fig 3. NO removal efficiency as a function of the ratio of concentrations of O_3 and NO

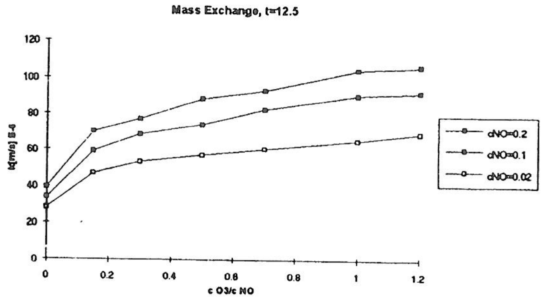
Complexity of the process makes theoretical calculations of absorption quantities practically impossible. That is why it seems to be purposeful to analyse the process on the basis of experimental results for to find significant dependences and distinguish reactions and phenomena that are of decisive character in the process. The aim of the research was to find a model relation including the process parameters and making possible to determine mass exchange coefficient (k_T).

Conclusions

1) The application of ozone for accelerating oxidation-absorption processes is one of possible indirect ways of removing nitrogen oxides from flue gases.

2) The performed experiments have proved that mass exchange coefficient in the process of NO absorption in water significantly grows as compared with analogous coefficient calculated for the conditions when only oxygen is used as an oxidizing

agent.. An analysis of the values of the k_T coefficient understood as a quantity that characterizes in a complex way the kinetics of the process make possible relative evaluation of the efficiency of ozone action as an oxidizer accelerating sorption process.



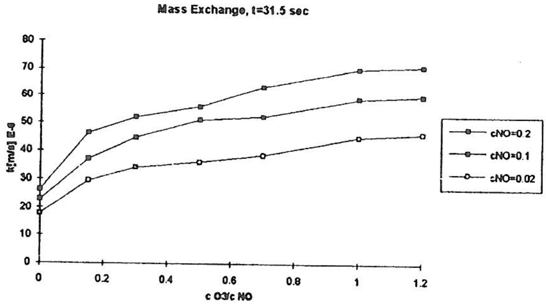


Fig 4. Mass exchange coefficient as a function of ratio of concentrations of O_3 and NO

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