

Oxidation of nitric oxide in a two-stage chemical scrubber using dc corona discharge

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Abstract

The dc corona was studied as an alternative for NO oxidation in a two-stage chemical scrubber. The dc corona plasma reactor completely oxidized 150 ppm of NO to NO₂ in an air stream. The NO₂ was further oxidized at a higher voltage. For some cases, the NO₂ in the effluents of the plasma reactor was absorbed quantitatively by a caustic sodium sulfite aqueous solution in a 21 bubble column gas absorber. The outlet concentrations of both NO and NO₂ from the plasma-scrubber combination system (corona-induced chemical scrubber) were below the detection limit of the chemiluminescent NO_x analyzer. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The oxides of nitrogen (NO_x) generated in high temperature operations are mainly nitric oxide (NO) and nitrogen dioxide (NO₂). NO₂ can be effectively absorbed in some aqueous solutions [1–3] but NO is not [4,5]. Unfortunately, most (more than 95%) of the NO_x emitted in flue gases are NO. Therefore, NO oxidation is a crucial step for a two-stage chemical scrubbing system, NO oxidation followed by NO₂ absorption, to be effective in NO_x emission control. The slow oxidation rate of NO in air can be improved by injecting a strong oxidizing agent such as ozone (O₃) [5], chlorine dioxide (ClO₂) [6,7] or chlorine (Cl₂) [8] into the flue gas or adding an oxidizing agent such as sodium chlorite (NaClO₂) [9–11], hydrogen peroxide (H₂O₂) [12], sodium hypochlorite (NaClO) [11,13,14] or potassium permanganate (KMnO₄) [5,14] to the scrubbing solution. In recent years, some two-stage chemical scrubbing systems have reached either pilot scale demonstration or full

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scale installation. Among them are hypochlorite/sulfide system from Tri-Mer [15] and from Environair [16], ozone/sodium hydroxide (NaOH) system from BOC-Cannon [17], chlorite/sulfite [18] and pulsed corona/sulfite systems from Yang and co-workers [19,20], and pulsed corona/thiosulfate system from ADA [18].

The oxidation of NO in the gas phase by O₃ or ClO₂ occurs much more rapidly than oxidation in the liquid phase because the rate of NO absorption in the aqueous solution is slow. O₃ is capable of oxidizing NO to not only to NO₂, but also to dinitrogen pentoxide (N₂O₅), which rapidly reacts with water or alkaline solutions to form nitric acid (HNO₃) or nitrates (NO₃⁻). BOC proposed the mechanism of NO oxidation with ozone as follow [17]:



The NO_x, primary NO and NO₂, is oxidized to higher oxidation state of N₂O₅ which is readily soluble in water. The N₂O₅ in the effluent of the oxidation stage is absorbed by the circulating water and is neutralized by NaOH in the second stage.

The overall reaction of NO with ClO₂ is as follow [7]:



The use of stoichiometric amount of ClO₂ oxidizes 95% NO in the gas in less than 2 s. Two Japanese studies confirmed the process in large gas flow rates, 300 and 70,000 m³/h. In both cases, the conversion of NO was about 90% [6].

The chlorine injection process for NO removal from gas streams was patented by Dow Company. This process consists of injection of Cl₂ into NO laden gas stream followed by rigorous scrubbing using an acid aqueous solution. The reaction by which the process is carried out is proposed as [8]



Also competing with Cl₂ for NO consumption is O₂ for the formation of NO₂ which then dissolves and reacts with hypochlorous acid (HClO) in water to form HNO₃



These reactions were found to be highly dependent upon gas stream Cl₂/NO ratio, temperatures and pH in the solution. More than 90% conversion is achievable.

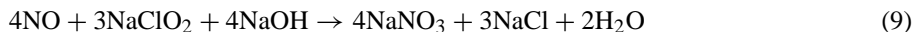
Several liquid-phase oxidants such KMnO₄, H₂O₂, NaClO and NaClO₂ were tested in two-stage chemical scrubbers for NO oxidation. Shaw [5] reported that a deposit of MnO₂ plated out on the wall of the scrubber. Experiments had to be stopped to prevent plugging of the liquid spray nozzle. Due to high decomposition rate, the H₂O₂ system requires careful handling and several times more chemical than stoichiometry [12]. These two processes were not further developed.

When dissolved in water, NaClO equilibrates with HClO and Cl₂ gas in the solution. Chironna and Altshuler [13] proposed the oxidizing reaction of NO with NaClO is as follows:

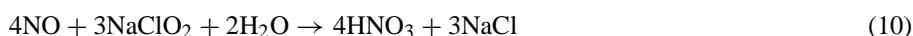


Yang et al. [11] found that the solution is most effective for NO oxidation in the range of pH 4 and pH 7 where HClO is the dominate component. More than 90% NO conversion is achievable. However, most of the NO is oxidized to NO₂ and remains in the gas phase.

Sada and Kumazawa [22] proposed that the oxidation of NO with NaClO₂ in the presence of NaOH can be represented by



Yang and Shaw [10] found that NaOH in the scrubbing solution inhibits NO oxidation. Therefore, most of their experiments were conducted with a neutral or slightly acid solution. Under these conditions, the overall reaction of NO with NaClO₂ was proposed as



In acid aqueous scrubbing, ClO₂ was found the active ingredient for NO oxidation. The greenish ClO₂ was identified and quantified using a UV/Vis range photodiode array detector in a preparatory liquid chromatography.

An alternative to chemical scrubbing processes is the corona-induced chemical scrubber [19–21]. This technology uses nonthermal plasma discharge in the first stage to oxidize NO to NO₂. With sulfite scrubbing in the second stage, exceptionally high NO_x removal rates of between 95 and 99% were achieved. Nonthermal plasma technologies have been investigated for control of NO_x emissions for years [23–28]. Previous studies show that more than 90% NO conversion is achievable. However, without adding reducing agent in the plasma discharge section, between 40 to 60% of the NO is oxidized to NO₂. The total NO_x reduction is only 55%, which is not much better than combustion modification and flue gas recirculation technologies alone.

The objective of the research presented in this paper is to study the dc corona discharge as an alternative for NO oxidation in a two-stage chemical scrubber. The dc corona has an advantage of being able to operate simultaneously as an electrostatic precipitator for particulate collection. The following scrubber is expected to remove all the undesired by-products, such as ozone, generated in the corona discharge section.

2. Experimental section

The bench scale tubular plasma reactor (TPR) test system is shown in Fig. 1. The system consists of a flue gas blending unit, a plasma reactor, a bubble column absorber, and a continuous NO_x analyzer. The Brooks mass flow controller is capable of producing a wide range variety of flue gas compositions by mixing components in different proportions. Both NO and NO₂ are derived from high-pressure cylinders, while the oxygen and nitrogen are from compressed air.

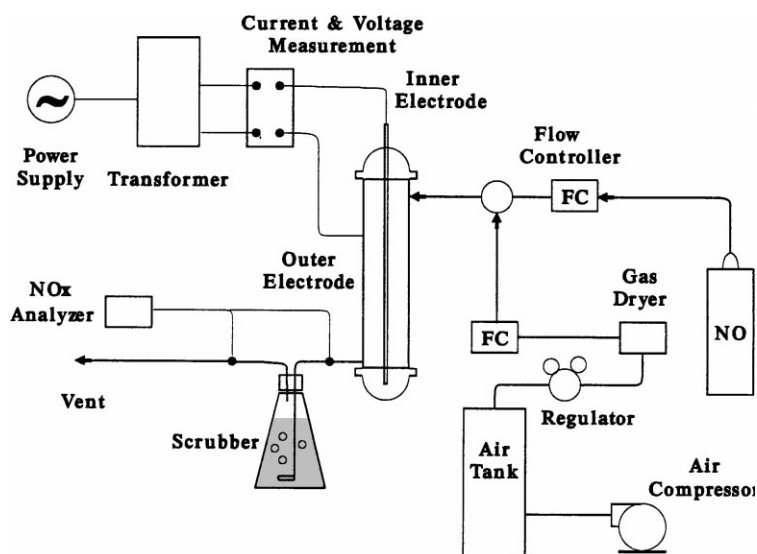


Fig. 1. Schematic of the corona-induced chemical scrubber test system.

2.1. Apparatus

The TPR is shaped like coaxial cylinders with an inner discharge electrode and an outer tube made of stainless steel. The reactor has a discharge gap of about 10 mm with a length of 300 mm. The inner electrode is connected to a high voltage (0–30 kV) dc power supply. The metal tube serves as the reaction vessel and a ground electrode. Fig. 2 shows how the TPR is constructed. The synthetic flue gas passes through the plasma reactor where NO is oxidized to NO_2 . The effluent gases are carried to the bubble column gas absorber where NO_2 is absorbed in the Na_2SO_3 aqueous solution. Gas samples are taken from the effluents of the plasma reactor and the gas absorber.

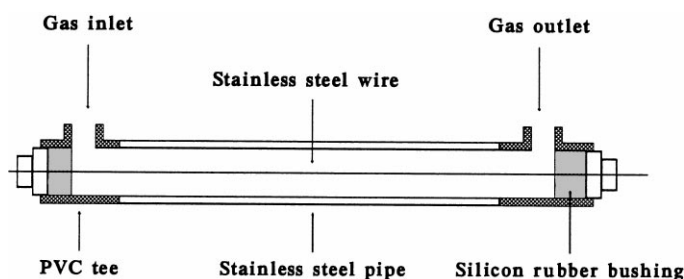


Fig. 2. The dc corona plasma reactor.

2.2. Analysis

An API 200AH NO_x analyzer is used to measure the concentrations of NO, NO_x and by calculation, NO₂ simultaneously. Signals from the NO_x analyzer come from the light emitted from the chemiluminescent gas phase reaction of nitric oxide and ozone. The reaction results in electronically excited NO₂ molecules. The excited NO₂ molecules release their excess energy by emitting a photon and dropping to ground state.

To measure NO concentration, the gas sample is blended with ozone in a reaction chamber. The ozone is generated in situ by a high-voltage arc ozone generator. The resulting chemiluminescence is monitored through an optical filter by a high sensitivity photomultiplier positioned at one end of the reaction chamber. The filter/photomultiplier combination responds to light in a narrow wavelength band unique to the second reaction. The output from the multiplier is linearly proportional to the NO concentration.

The chemiluminescent analysis is only sensitive to NO. To measure NO_x concentrations, the sample gas is diverted through a high temperature converter, where the NO₂ is converted to NO and the total of NO_x, NO plus NO₂ is detected as NO. The NO₂ concentration is the difference between the two readings for NO_x and NO. Signals from the NO_x analyzer are continuously recorded.

3. Results and discussion

The results of the bench-scale research program are given in this section. Corona characteristics, NO₂ formation in plasma reactors, NO oxidation with respect to applied voltages were studied. The concept of oxidizing NO in the corona discharge section followed with the absorption of NO₂ was confirmed.

3.1. Corona characteristics

A thorough study of corona characteristics should include corona current in the concentric-cylinder electrodes, the effects of wire and cylinder diameters, voltage waveforms, gas pressure and temperature and gas compositions. In this study, only corona currents versus applied voltages were measured in order to evaluate the power consumption. Corona current was measured by connecting an ammeter in series with the plasma reactor. Experiments were conducted under the following conditions:

- reactor: 20 and 51 mm ID, 300 mm long stainless steel pipe;
- discharge electrode: 1.6 mm stainless steel wire;
- voltage applied: 0–25 kV dc;
- loading: 2 l/min dry air.

Fig. 3 shows the typical curves of the corona current of a 20 mm ID and 51 mm ID plasma reactor driven by a dc power supply. The small reactor started to draw current at a voltage of 7 kV and sparked over at 13.5 kV. Up to spark-over, the reactor draws a maximum current of 500 μA. A similar characteristic was observed in the 51 mm reactor.

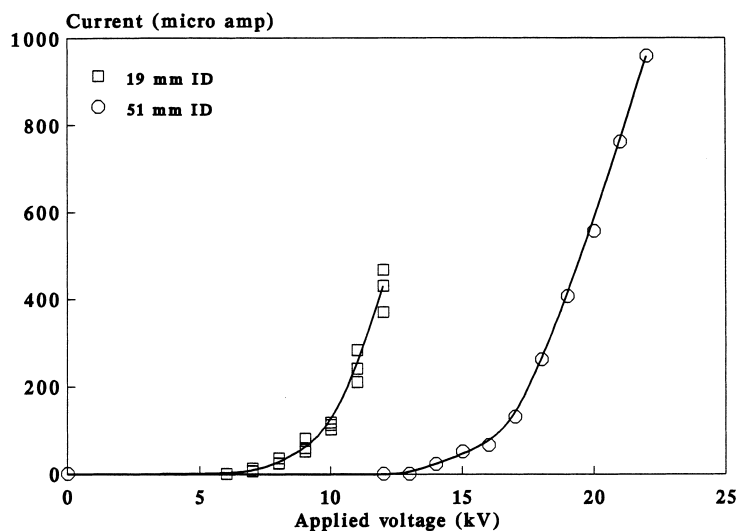


Fig. 3. Corona characteristics of plasma reactor.

3.2. Formation of NO_2

Nonthermal plasmas were once called cold combustion. This refers to their ability to produce active species by energy discharge as combustion does. Since the two major components in air are nitrogen and oxygen, there is a good reason to believe that a plasma reactor will produce a certain amount of nitrogen oxides in its operation. A literature review reveals that oxides of nitrogen are always among the undesired byproducts in plasma technologies for VOC destruction [19,20]. Tests presented in this section were designed to identify the species of nitrogen oxides (NO and NO_2) produced in the plasma reactor and to quantify their equilibrium concentrations. Experiments were conducted under the following conditions:

- reactor: 20 mm ID, 300 mm long stainless steel pipe; 20 mm ID, 275 mm long Pyrex glass column with and without glass beads;
- discharge wire: 1.6 mm stainless steel wire;
- voltages applied: 0–16 kV ac or dc;
- loading: 2 l/min dry air.

Fig. 4 shows the concentrations of NO_2 as a function of residence time and voltages applied on the plasma reactors. The curve indicated with TPR-ac represents the concentration of NO_2 produced with high voltage ac current in the empty Pyrex glass reactor. CPR-glass is the glass reactor packed with 6 mm glass beads and TPR-dc is the metal reactor energized with dc current. A 2 l/min flow rate to the system represents a residence time of 2.9 s. Since the plasma reactors producing significant amount of NO_2 but not producing NO , the idea of reducing NO to N_2 and O_2 in plasma reactor might not be feasible without adding a reducing agent in the system. However, the idea of converting NO to NO_2 for chemical scrubbing is promising.

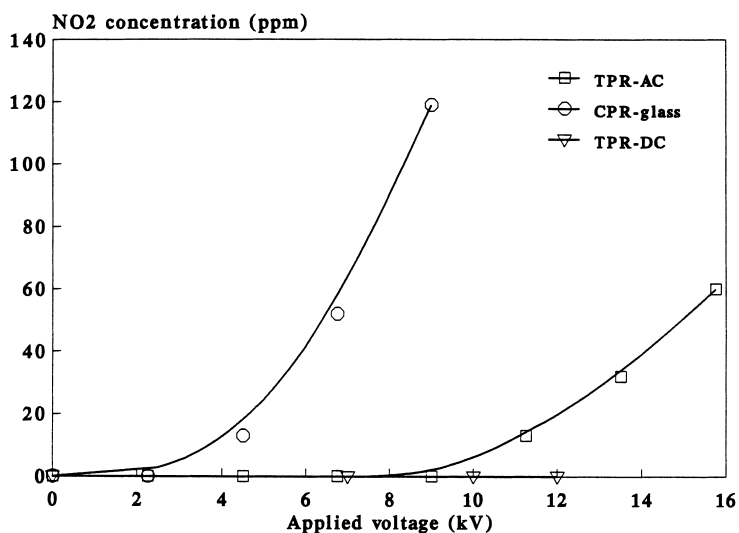


Fig. 4. Formation of NO_2 in plasma reactors.

3.3. NO oxidation with dc corona

The dc corona plasma reactor was tested for the feasibility of NO oxidation. A number of tests were performed at a NO_x concentration of 200 ppm, which is in the range of uncontrolled combustion or incineration sources. The inlet concentration of NO was adjusted by mixing 10% NO from the high-pressure cylinder with dry compressed air. The NO_2 in the inlet stream was produced in the mixer by mixing high concentration NO with air. The API 200AH NO_x analyzer was used to measure the concentrations of NO and NO_x directly and to calculate the concentrations of NO_2 . All of these concentrations were recorded continuously with a strip chart recorder. Experiments were conducted under the following conditions:

- reactor: 20 mm ID, 300 mm long stainless steel pipe;
- discharge electrode: 1.6 mm stainless steel wire;
- voltage applied: 0–13 kV dc;
- loading: 1.5 l/min, 150 ppm NO and 50 ppm NO_2 .

Fig. 5 shows the outlet concentrations of NO, NO_2 and NO_x as a function of voltages applied to the reactor. Up to 9 kV, NO_x conversion remained less than 10%. At a voltage of 10 kV, more than 90% of NO were oxidized to NO_2 . The outlet NO_2 made up to 90% of the outlet NO_x concentration. Beyond 10 kV, the total NO_x began to decline. At a voltage of 11 kV, all of the NO was oxidized to NO_2 and the concentration of total NO_x was reduced to 25% of the inlet concentration. Up to 13 kV, all of the inlet NO and NO_2 disappeared from the NO_x analyzer. Since this is an oxidizing process, it is believed that all the NO and NO_2 were oxidized to nitrate.

In view of the results presented in the previous section, it became apparent that the dc corona was effective for low concentration NO oxidation. A test was made to evaluate the

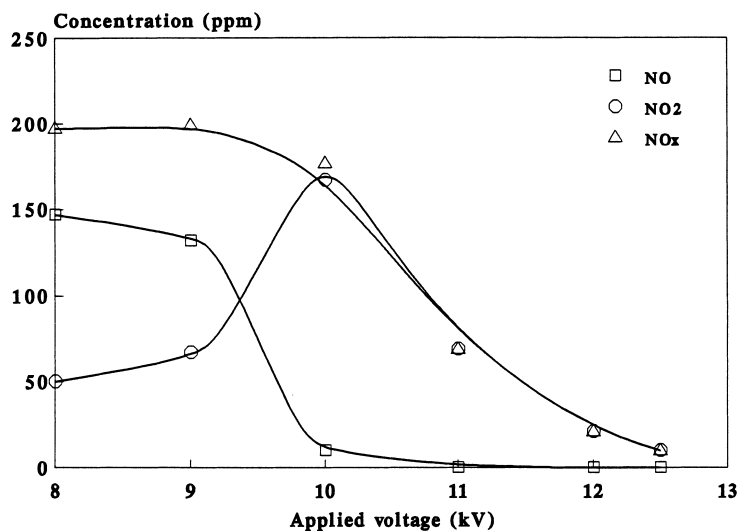


Fig. 5. Oxidation of low concentration (200 ppm) NO_x in a dc corona plasma reactor.

effectiveness of converting high concentration NO to NO_2 . The inlet concentration was set at 620 ppm. Fig. 6 shows the outlet concentrations of NO, NO_2 and NO_x from the corona discharge section. Both NO and NO_2 concentrations dropped to beyond detection limit right before the spark-over which was at 13.5 kV.

A flow rate of 1.51 per minute in the plasma reactor represents a residence time or treatment time of 3.8 s. The system was barely able to treat an inlet NO_x of 600 ppm to

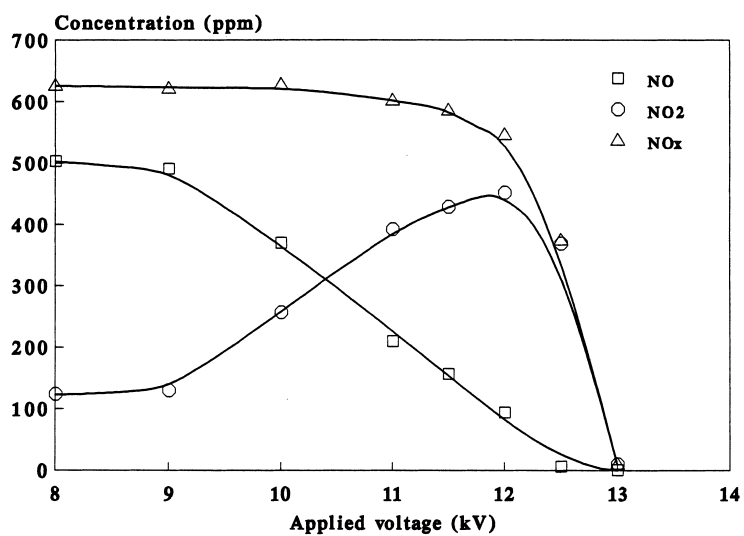


Fig. 6. Oxidation of high concentration (620 ppm) NO_x in a dc corona plasma reactor.

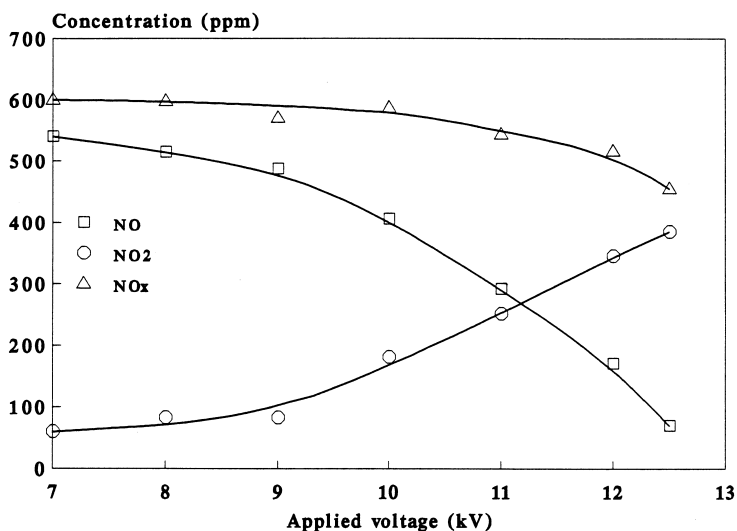


Fig. 7. Oxidation of nitrogen oxides in a 20 mm ID plasma reactor at 2 l/min.

<1 ppm. An intention of the following experiment was to reduce treatment time. A test of NO_x oxidation was performed at a flow rate of 2 l/min, which represents a residence time of 2.9 s. Fig. 7 shows the outlet concentrations of NO, NO₂ and NO_x with respect to voltages applied to the reactor. The plasma reactor oxidized more than 90% of the NO to NO₂. Up to spark-over, it failed to further oxidize the NO₂.

One way of producing high energy electrons and avoiding pre-mature spark-over at low voltage is to increase the discharge gap of the plasma reactor. A plasma reactor with a diameter of 51 mm was constructed to repeat previous experiment. In this reactor, a flow rate of 2 l/min represents a residence time of 18.5 s. The corona characteristics of the reactor are depicted in Fig. 3. Fig. 8 shows the test results of the 51 mm reactor for NO_x oxidation. Up to 23 kV, the reactor oxidized all 550 ppm NO to NO₂. However, the overall NO_x conversion was only 50%. Clearly, increasing reactor diameter is not the right way of scaling-up a plasma reactor.

3.4. Corona-induced chemical scrubber

The concept of a corona-induced chemical scrubber is to oxidize NO to NO₂ with corona discharge and then absorb the NO₂ in sodium sulfite aqueous solutions. As stated in the previous section, the plasma discharge oxidized NO to NO₂ effectively. A bubble column scrubber was installed downstream of the plasma reactor to confirm the idea of combining plasma discharge and chemical absorption for NO_x control. Sampling ports were set up between the plasma reactor and the chemical scrubber and right after the scrubber, as shown in Fig. 1. Experiments were conducted under the following conditions:

- reactor: 20 mm ID, 300 mm long stainless steel pipe;
- discharge electrode: 1.6 mm stainless steel wire;

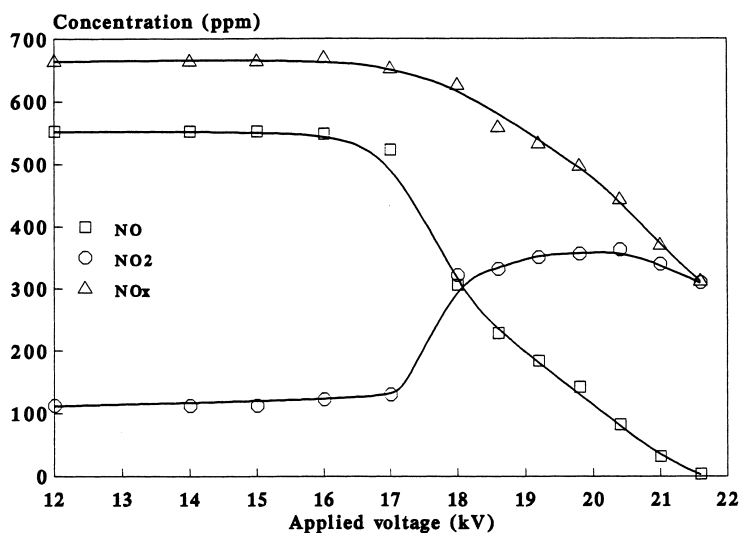


Fig. 8. Oxidation of nitrogen oxides in a 51 mm ID plasma reactor.

- voltage applied: 0–16 kV dc;
- loading: 2 l/min dry air, 120 ppm NO, 20 ppm NO₂;
- scrubber: 2 l gas washing bottle;
- scrubbing solution: 5% by weight of both Na₂SO₃ and NaOH in water.

Fig. 9 shows the outlet concentrations of NO, NO₂ and NO_x of the plasma reactor except for the curve indicated by NO_x-SCB, which is the NO_x concentration in the effluent of

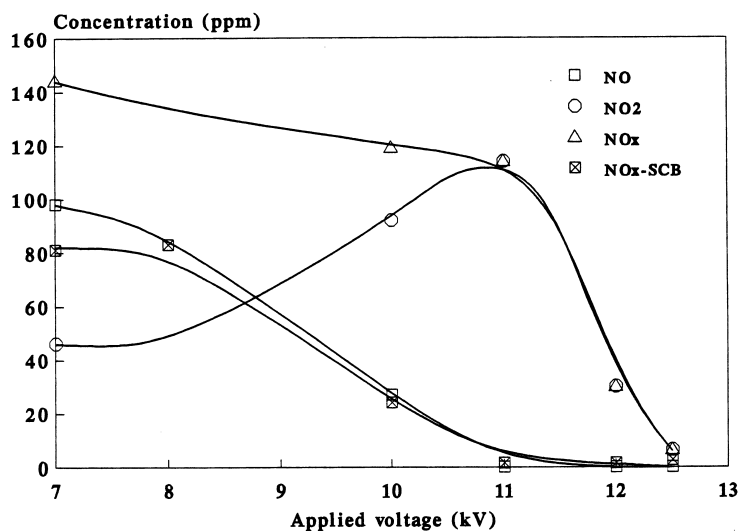


Fig. 9. Removal of nitrogen oxides in a corona-induced chemical scrubber at 2 l/min.

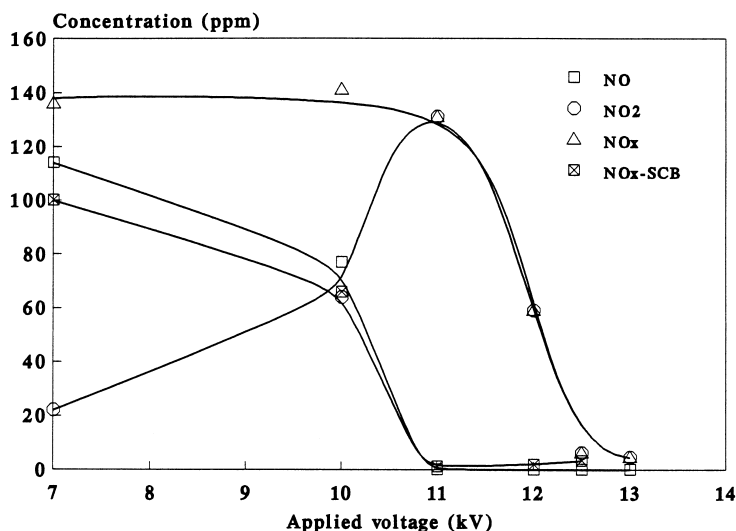


Fig. 10. Removal of nitrogen oxides in a corona-induced chemical scrubber at 4 l/min.

the chemical scrubber. The concentration profile is similar to that in the previous section, with a 2 kV shift to the high voltage side. This is because of the short residence time. The concentrations of NO are superimposed on the curve indicated as NO_x-SCB, which means the scrubbing solution is effective in NO₂ absorption.

Another set of tests was made to further lower the treatment time. The same experiment was repeated in the plasma reactor with a loading of 4 l/min which represents a residence time of 1.44 s. Fig. 10 shows the concentrations of nitrogen oxides from the plasma reactor and the combined system. The system successfully oxidized both NO and NO₂ to nitrate right before spark-over. The operating voltages between complete conversion and spark-over was minimal. This will not affect the removal efficiency of the corona-induced chemical scrubber. However, this will increase the difficulty of the electronic control of the dc power supply.

4. Conclusions

The concept of corona-induced chemical scrubber has been confirmed to be very effective for NO_x removal. The dc corona was able to convert NO to NO₂ effectively while sodium sulfite was found effective for NO₂ absorption. The outlet concentrations of both NO and NO₂ from the plasma-scrubber combination system (corona-induced chemical scrubber) were below the detection limit of the chemiluminescent NO_x analyzer.

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