Removal of NO by a Pulsed-Corona Reactor Combined with In Situ Absorption

Liwei Huang
College of Biological and Environmental Engineering, Zhejiang University of Technology, Hangzhou 310032, China

Hitoki Matsuda
Research Center for Advanced Waste and Emission Management, Nagoya University, Nagoya 464-8603, Japan

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Removal of NO by nonthermal plasma, combined with in situ absorption, was experimentally investigated with a wire-in-tube pulsed-corona reactor. High pulse voltage was applied to the wire of the reactor and the tube was grounded. For the reactor combined with in situ absorption, the grounding electrode was covered by a $Ca(OH)_2$ layer as the sorbent for in situ capture of the NO oxidation products. It was found that NO removal was much higher by the reactor combined with in situ absorption than by the reactor without $Ca(OH)_2$ sorbent and, meanwhile, the outlet NO_2 concentration from the reactor was also suppressed to less than 10 ppm. It was indicated that in situ absorption of the NO_2 by $Ca(OH)_2$ was responsible for the promotion of NO removal. The existence of O_2 and water vapor in the gas stream is beneficial for NO oxidation, therefore resulting in the significant increase of NO removal. © 2004 American Institute of Chemical Engineers *AIChE J,* 50: 2676–2681, 2004

Keywords: nonthermal plasma, corona reactor, NO_x, absorption, removal

Introduction

Nitrogen oxides (NO_x), including nitrogen oxide (NO) and nitrogen dioxide (NO_2), are generated from fuel combustion and industrial processes. The emission of NO_x into the atmosphere is one of the factors responsible for acid rains and atmospheric photochemical smog (Singh, 1987; Spengler et al., 1990). Generally, there are two processes categorized as dry and wet technologies for the removal of NO_x from gas streams (Bradford et al., 2002). Selected catalytic reduction (SCR) is a major dry process for postcombustion NO_x treatment, but it requires strict operation conditions such as reaction temperature and gas compositions. Wet processes use aqueous solutions for NO_x absorption, but to find a medium for economical and effective removal of NO is still a challenging work, and the disposal of the spent solutions may become an additional problem.

Nonthermal plasma generated by pulsed-corona and dielectric barrier discharges has been regarded as an alternative method for NO_x removal (Chang et al., 1992; Matsuda and Nakao, 1990; Mclarnon and Mathur, 2000; Penetrante et al., 1995; Young et al., 2000). Previous studies showed that the removal of NO under nonthermal plasma undergoes both reduction and oxidation processes (Chen and Mathur, 2002; Gentile and Kushner, 1995; Sathiamoorthy et al., 1999). It was demonstrated that, in an oxidizing atmosphere, the oxidation reaction of NO to NO_2 dominates the NO removal process and correspondingly, NO removal prefers to undergo a reduction process to N_2 in a reducing atmosphere (Huang et al., 2001). However, because nonthermal plasma–induced chemical reactions are very difficult to control, many methods have been developed to control the conversion of NO with reaction additives and/or other chemical processes (Chang and Yang, 2001; Mizuno et al., 1995; Niessen et al., 1998; Shimizu et al., 2001; Yang et al., 1998).

Correspondence concerning this article should be addressed to L. Huang at hliwei@mail.hz.zj.cn.

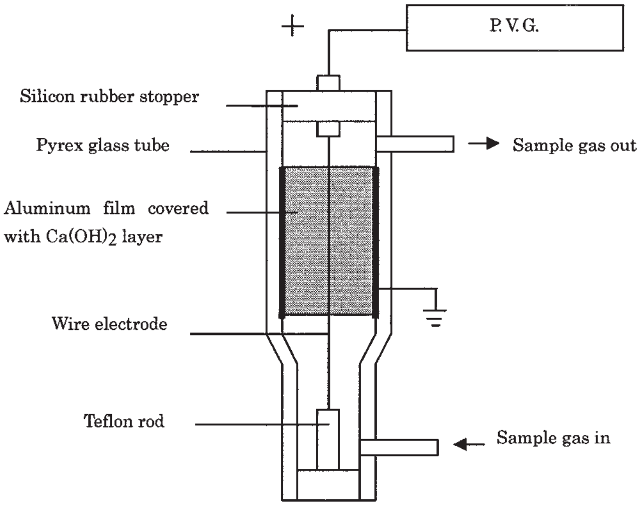

Figure 1. Pulsed corona reactor.

In this study, a novel technique of nonthermal plasma combined with in situ gas absorption is devised for NO removal. In a pulsed-corona reactor, a porous layer of calcium hydroxide is coated on the grounding electrode. When the gas stream goes through the plasma zone between the two electrodes, the NO will be oxidized to NO_2 by plasma chemical reactions, and then the produced NO_2 is captured by the $Ca(OH)_2$ layer in the reactor.

Experimental Design

The wire-in-tube corona reactor is shown in Figure 1. It consists of a Pyrex glass tube with an aluminum film tightly attached to the inner wall as the grounding electrode and a coaxial stainless steel wire of 0.5 mm in diameter as the corona wire. The inner diameter of the tube is 28 mm. The aluminum film is 0.3 mm thick and 300 mm long. For the corona reactor combined with in situ absorption, a $Ca(OH)_2$ layer of about 1 mm thickness was coated on the grounding electrode, the surface of the aluminum film. To make the $Ca(OH)_2$ coated electrode, a $Ca(OH)_2$ slurry, prepared by mixing 60% water and 40% $Ca(OH)_2$ powder, was evenly painted on the aluminum film of the grounding electrode. After the $Ca(OH)_2$ layer was naturally dried in air for about 1 h, the whole reactor was placed in an electric stove for heating at 110°C in air for 3 h to form the electrode. The mass of $Ca(OH)_2$ layer was 40 g.

A typical pulse-forming circuit, using a rotating spark gap (RSG) system, was adopted to produce the pulsed voltage as the schematic circuit shown in Figure 2. It consists of two parts: a high dc-forming circuit and a pulse-forming circuit. A capacitor C was charged by high dc supply through resistor R. When the RSG reached the point of conduction, the energy stored in the capacitor was injected into the reactor. It was measured that the width of the voltage pulse was less than 300 ns, and that the rising time was within 50 ns. The pulse repetition rate was set at 50 pulses/s. The energy injected into the reactor was calculated by measuring the voltage and current waveforms. The influences of the $Ca(OH)_2$ layer on the discharge characteristics were also measured. We did not find obvious changes in current and voltage waveform with the coating except that the onset discharge voltage increased slightly.

A pressurized gas cylinder of standard NO concentration of 2000 ppm in N_2 was used in the experiment to make the sample NO concentration of 800 ppm by mixing N_2 and O_2 gas before feeding into the reactor. The total flow rate of gas was fixed at a constant value of 500 cm^3/min for all experiments. Analyses of the gas sample, before and after reaction, were carried out by a chemiluminescence NO_x analyzer (Yanaco, ECL-88A0). The removal of NO is defined as

$$\eta = \frac{C_{in} - C_{out}}{C_{in}} \times 100\% \qquad (1)$$

where C_{in} and C_{out} are the inlet concentration of NO and outlet concentration of NO, respectively.

Results and Discussion

Removal of NO in pure N_2

Reactions 2–5 are regarded as constituting the mechanism for the nonthermal plasma depletion of NO in N_2 atmosphere (Penetrante et al., 1995)

$$e + N_2 \rightarrow e + N + N \qquad (2)$$

$$N + NO \rightarrow N_2 + O \qquad (3)$$

$$O + NO + M \rightarrow NO_2 + M \qquad (4)$$

$$NO_2 + N \rightarrow 2NO \qquad (5)$$

The N atoms required for the reduction of NO by reaction 3 are produced by the electron-impact dissociation of the N_2 molecule. A number of NO molecules may be oxidized to NO_2 by the produced O atoms by reaction 4. Meanwhile the product of NO_2 may convert back to NO again by reaction 5.

Figure 3 shows the removal of NO in pure N_2 gas as a function of the applied pulse voltage (peak) varying from 16 to 22 kV (corresponding to the power injection of about 200 to 900 J/L into the reactor). The initial concentration of NO is 800 ppm. Without the plasma on, the concentrations of nitrogen oxide at both inlet and outlet of the corona reactor were the same, irrespective of whether $Ca(OH)_2$ was present in the reactor. NO could not be removed by the calcium hydroxide

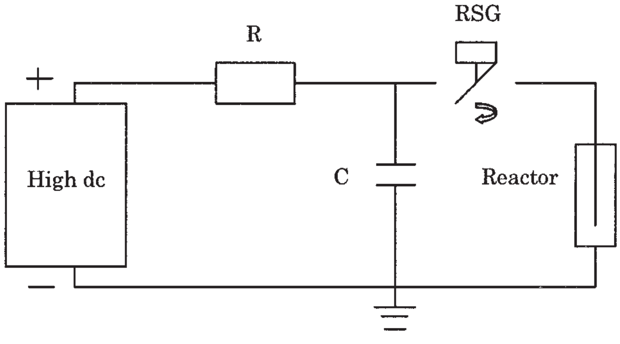

Figure 2. Pulse-forming circuit.

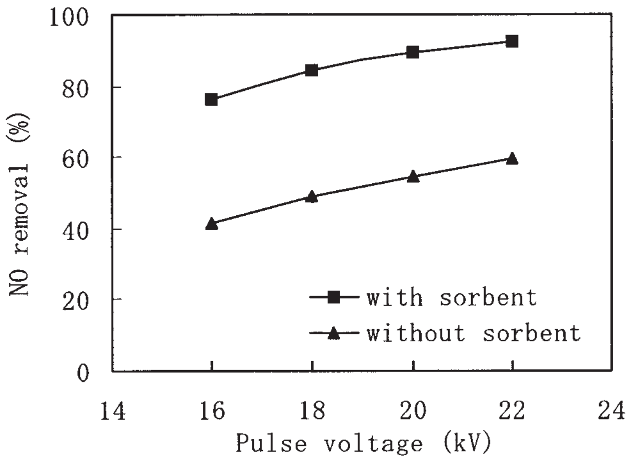

Figure 3. NO removal as a function of pulse voltage.
In N_2; NO: 800 ppm.

layer alone because the reaction between nitrogen oxide and calcium hydroxide does not occur. In Figure 3, the curve above represents the NO removal by the reactor combined with $Ca(OH)_2$ absorption, and the curve below is the NO removal by the reactor without the $Ca(OH)_2$ layer. It was found that the removal of NO increased from 76% (energy cost for NO removal is 15 g/kWh) to 93% (energy cost is 4 g/kWh) with the increase of the pulse voltage from 16 to 22 kV by the reactor with in situ $Ca(OH)_2$ absorption, which was much higher than that by the reactor without the $Ca(OH)_2$ layer. On the other hand, the outlet concentration of NO_2 showed substantial difference under these two conditions, as given in Figure 4. It was observed that the outlet concentration of NO_2 was around 10 ppm for the reactor with the $Ca(OH)_2$ layer, and for the reactor without $Ca(OH)_2$ sorbent, the outlet NO_2 concentration increased to around 80 ppm. This indicated that the $Ca(OH)_2$ layer in the reactor played an important role in promoting the removal of NO, and meanwhile subdued the production of NO_2.

The solid products were analyzed to find evidence of the participation of $Ca(OH)_2$ in the NO removal process. After the reaction, a portion of the sorbent was collected from the surface layer on the grounding electrode. The sorbent was dissolved in water, and an ion chromatograph was used to detect the ion composition in the water solution. Ion analysis showed the presence of NO_2^- and NO_3^- ions in the water solution. This result indicated that the $Ca(OH)_2$ sorbent participated in the removal of NO by in situ capturing NO_2 to form the products of $Ca(NO_2)_2$ and $Ca(NO_3)_2$ by reaction 6. Therefore, NO removal was promoted by removing the product of NO_2 from the right side of reaction 4 and suppressing the product of NO_2, converting back to NO again, by reaction 5

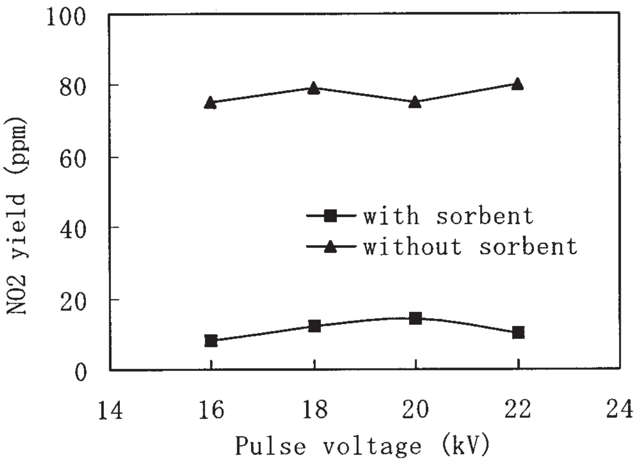

Figure 4. NO_2 yield as a function of pulse voltage.
In N_2; NO: 800 ppm.

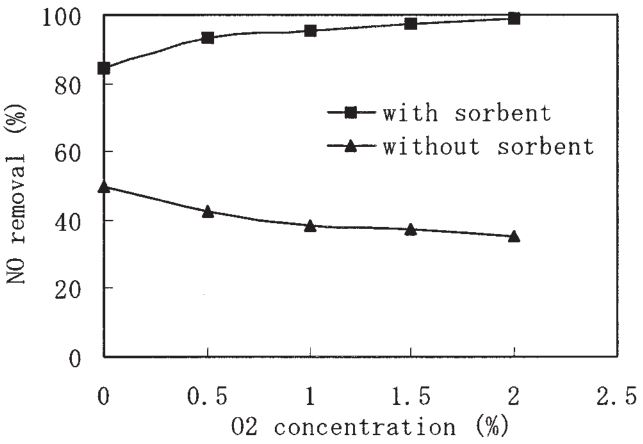

Figure 5. Influence of O_2 concentration on NO removal.
V_p: 18 kV; NO: 800 ppm.

$$2Ca(OH)_2 + 4NO_2 \rightarrow Ca(NO_3)_2 + Ca(NO_2)_2 + 2H_2O \tag{6}$$

Influence of O_2 concentration on NO removal

With the presence of O_2 in the gas stream, the removal of NO may occur readily by oxidation pathway, in conformity with reactions 4 and 7. However, the N atoms used to reduce NO may be competitively consumed by reaction 8 to produce NO, and the produced NO_2 may be reduced back to NO by reaction 9, which may result in a decrease in the conversion of NO (Gentile and Kushner, 1995)

$$NO + O_3 \rightarrow NO_2 + O_2 \tag{7}$$

$$N + O_2 \rightarrow NO + O \tag{8}$$

$$NO_2 + O \rightarrow NO + O_2 \tag{9}$$

Figures 5 and 6 show the influence of the O_2 concentration on NO removal and NO_2 yield, respectively. The pulse voltage applied to the reactor was fixed at 18 kV (400 J/L). It can be seen that without the $Ca(OH)_2$ sorbent in the reactor, the NO removal decreased from 50 to 35%, and meanwhile NO_2 production increased from 79 to 147 ppm with increasing O_2 concentration, from zero to 2%, in the gas stream. Previous researchers Chang et al. (1992) and Chen and Mathur (2002) also reported the negative effect of O_2 concentration on NO removal in N_2. On the other hand, for the reactor with $Ca(OH)_2$

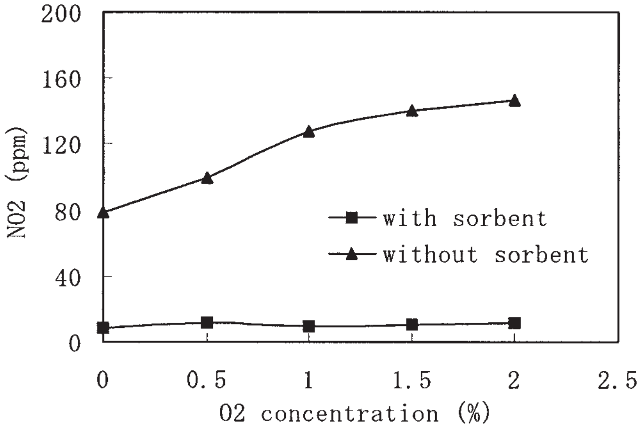

Figure 6. Influence of O_2 concentration on NO_2 yield.

V_p: 18 kV; NO: 800 ppm.

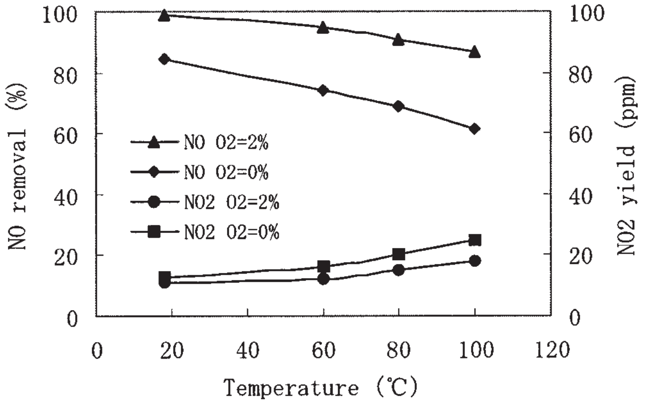

Figure 7. Influence of reaction temperature on NO removal.

V_p: 18 kV; NO: 800 ppm.

sorbent, NO removal showed the opposite result. Removal of NO increased with increasing O_2 concentration in the gas stream, and NO removal of 100% was achieved when the O_2 concentration increased to 2%. Compared with the NO_2 yield without sorbent in the reactor, the outlet NO_2 concentration was less than 10 ppm, regardless of the concentration of O_2 in the gas stream. These results demonstrate that with the presence of O_2 in gas stream, the oxidation removal of NO was significantly increased by the reactor with in situ $Ca(OH)_2$ absorption.

Influence of gas temperature on NO removal

In a nonthermal plasma, the electron-impact dissociation or ionization of the background gases is almost independent of gas temperature. However, the reactions between produced radicals and targeted molecules may be dependent on gas temperature. For the gas temperature changing from room temperature to 100°C, the influence of gas temperature on NO removal may be neglected (Penetrante et al., 1995), although in our case, for the reactor combined with in situ absorption, the gas–solid reaction may be influenced by increasing gas temperature, which may result in the decrease of NO removal, as shown in Figure 7. It was found that the removal of NO decreased from 100 to 85% in a gas mixture of 2% O_2 and 98% N_2 as the gas temperature increased from room temperature (20°C) to 100°C. On the other hand, the outlet NO_2 concentration of the reactor also increased with increasing gas temperature. In fact, according to chemical thermodynamics, the product of $Ca(NO_3)_2$ will be decomposed back to NO_2 at temperatures above 500°C (Gordon and Campbell, 1955), which may be used to regenerate the sorbent. We performed the experiment by putting the reactor into a cylindrical electric stove and raising the temperature of the reactor. The release of NO_x from the reactor was detected when the reactor temperature was above 200°C.

It should be mentioned that the NO_2 absorption reaction would last until the sorbent of $Ca(OH)_2$ is exhausted. In the whole experiment, we did not find that the $Ca(OH)_2$ layer became ineffective, given that only a very small part of $Ca(OH)_2$ participated in the absorption reaction, compared with the removed NO_2 in the gas stream. With progression of this process, the sorbent will gradually become deactivated, although this process takes a long time.

Influence of water vapor

In the absence of H_2O, the dominant reaction for NO reduction in N_2 is reaction 3. With the presence of water vapor in the gas stream, the electron-impact dissociation of H_2O may provide oxidative radicals of OH and HO_2, which may oxidize the NO to NO_2 and HNO_2 by reactions 11 and 12

$$e + H_2O \rightarrow e + H + OH \tag{10}$$

$$NO + HO_2 \rightarrow NO_2 + OH \tag{11}$$

$$NO + OH \rightarrow HNO_2 \tag{12}$$

Figures 8 and 9 show the removal of NO and the yield of NO_2, respectively, as a function of pulse voltage in the presence of water vapor in the gas stream (800 ppm NO in N_2 gas). The addition of water vapor into the stream was achieved by introducing the sample gas through a water bubbler before the

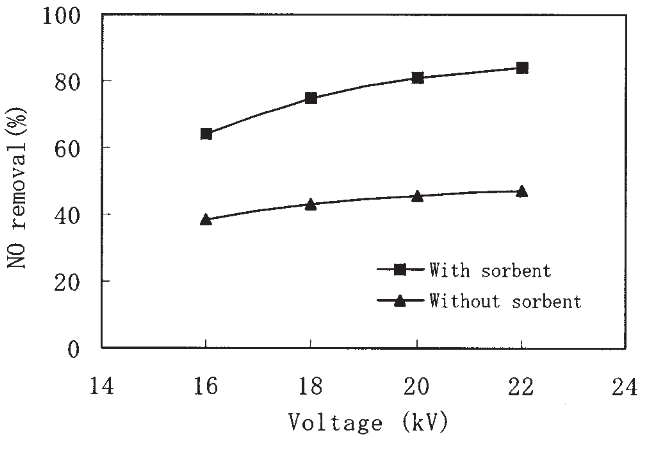

Figure 8. Influence of water vapor on NO removal.

Water vapor: 10%; in N_2; NO: 800 ppm.

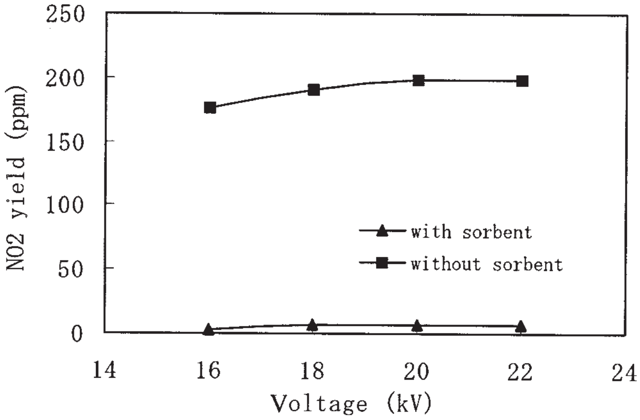

Figure 9. Influence of water vapor on NO_2 yield.

Water vapor: 10%; in N_2; NO: 800 ppm.

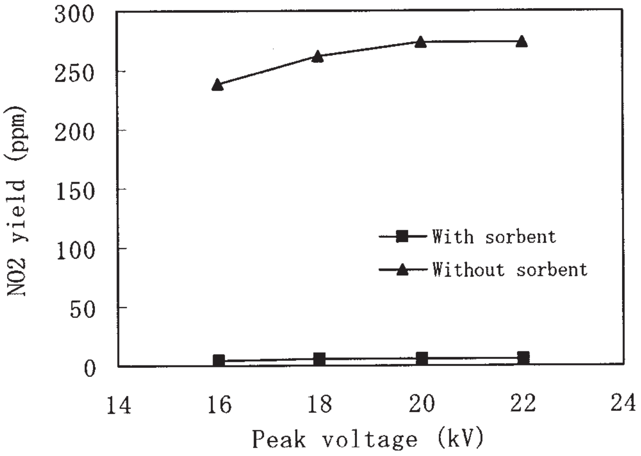

Figure 11. Influence of water vapor on NO_2 yield.

Water vapor: 10%; in 2% O_2/98% N_2; NO: 800 ppm.

corona reactor. The content of water vapor in the gas stream was adjusted to 10%. Compared with results shown in Figures 3 and 4, the presence of water vapor in the stream resulted in the decrease of NO removal. It is thought that the dissociation attachment of H_2O consumes an amount of energetic electrons that would contribute to the production of N radicals. Therefore, the reduction of NO by N was inhibited (Chen and Mathur, 2002). On the other hand, the production of NO_2 increased, as shown in Figure 8. This result demonstrated that the presence of water vapor in the gas stream contributed to the oxidation of NO to NO_2. It was also found that with the $Ca(OH)_2$ sorbent in the reactor, the removal of NO was also higher than that by the reactor without $Ca(OH)_2$ sorbent; on the other hand, the outlet NO_2 was almost close to zero.

Figures 10 and 11 show the removal of NO and the production of NO_2 with the addition of water vapor in the gas mixture of 2% O_2 and 98% N_2, respectively. Compared with results shown in Figures 5 and 6, without $Ca(OH)_2$ sorbent in the reactor, the presence of water vapor in the gas stream did not cause decreased NO removal, although the NO_2 production was substantially increased, which indicated that the presence of water provided additional oxidation channels for the process of NO removal. With the $Ca(OH)_2$ sorbent in the reactor, the NO removal dramatically increased to almost complete decomposition. It was also found that the outlet NO_2 concentration was considerably lower, compared with the result without water vapor in the gas stream. This outcome shows that the presence of water vapor in the gas stream might be beneficial for NO_2 absorption.

The above experimental results verify that the production of NO_2 is an essential step for NO removal. The gas–solid reaction between the product NO_2 and $Ca(OH)_2$ seemed sufficiently fast to remove NO_2 in the gas phase, compared with the conversion of NO to NO_2. The outlet NO_2 concentrations were almost stable with increasing energy injection into the reactor. When oxygen and water were present in the gas stream, to increase the production of NO_2, NO removal increased.

Corona reactor with downstream absorption

As a comparison, NO removal by the corona reactor, combined with downstream absorption, was also carried out. A $Ca(OH)_2$ packed-bed absorber was connected just after the gas left the corona reactor for removal of the NO_2 product. The diameter of this tube absorber is the same as that of the corona reactor. In the absorber, the $Ca(OH)_2$ packed bed is 20 mm in

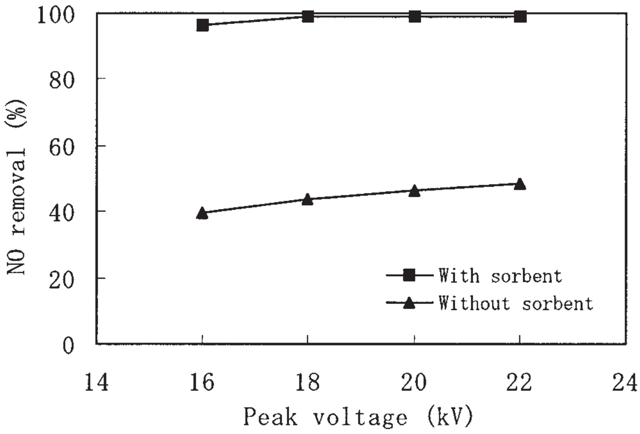

Figure 10. Influence of water vapor on NO removal.

Water vapor: 10%; in 2% O_2/98% N_2; NO: 800 ppm.

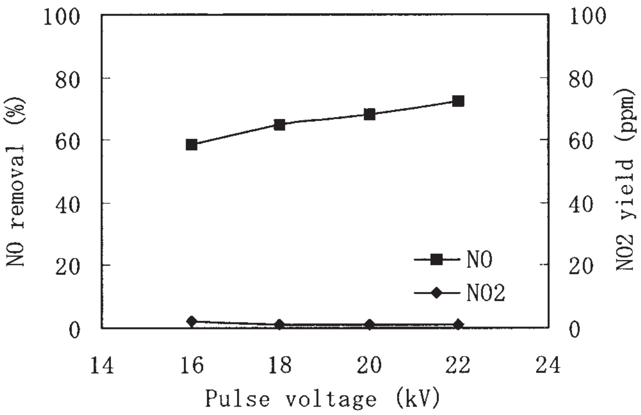

Figure 12. NO removal with downstream absorption.

Water vapor: 10%; in 2% O_2/98% N_2; NO: 800 ppm.

height above a glass gas distributor. Other operation conditions are as same as those used for the experiments shown in Figure 10. By comparing the result shown in Figure 12 with that in Figure 10, it was found that the NO_2 concentration outlet of the absorber almost approached zero, but the NO removal decreased by 30%. It is determined that with such a combination, the product of NO_2 was removed by the $Ca(OH)_2$ sorbent in the absorber, but the unreacted NO could not be removed. In other words, the plasma reaction for NO removal was unable to proceed by installing an absorber downstream of the reactor.

Conclusions

Removal of NO by a wire-in-tube pulsed-corona reactor with in situ absorption was experimentally investigated. The result shows that nonthermal plasma with in situ absorption is an effective way to remove NO in the gas stream. Compared with the result by the reactor without sorbent, NO removal was much higher by the reactor with a $Ca(OH)_2$ layer on the grounding electrode. It was demonstrated that gas–solid absorption reactions between produced NO_2 and $Ca(OH)_2$ caused an increase of NO removal in the reactor. The existence of O_2 and water vapor in the gas stream was beneficial for NO oxidation, therefore resulting in a significant increase in NO removal. NO removal of 100% was achieved for 800 ppm NO in a gas mixture of 2% O_2 and 98% N_2 with a pulse voltage of 18 kV. The solid products were confirmed to exist in the form of $Ca(NO_2)_2$ and $Ca(NO_3)_2$.

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