# Simultaneous removal of NO and SO$_2$ from dry gas stream using non-thermal plasma

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## Abstract

In order to investigate the feasibility of sequential removal NO and SO$_2$ using non-thermal plasma and adsorbent simultaneously, the removal of NO and SO$_2$ from dry gas stream (NO/SO$_2$/N$_2$/O$_2$) with very little O$_2$ using non-thermal plasma was investigated using a coaxial dielectric barrier discharge. Comparative experiments were carried out in the dry gas stream with and without Ar respectively at O$_2$ concentration of 0.1%. The results showed that NO could be removed remarkably and it would be enhanced in the presence of Ar in the dry gas stream. It seems that SO$_2$ could not be removed unless there is Ar in the dry gas stream. The mechanism of removal of NO and SO$_2$ in the dry gas stream was discussed.

**Key words**: NO; SO$_2$; non-thermal plasma; dry gas stream; simultaneous removal

## Introduction

The simultaneous removal of NO and SO$_2$ emitted from coal combustion boiler has become an important issue because of stringent limits imposed on the allowable levels of NO and SO$_2$ emissions (Jin *et al.*, 2006).

Some of the new methods being investigated for post-combustion removal of NO and SO$_2$ are based on the non-thermal plasma. Several successful demonstrations in power plants have been set up with the De-NO and De-SO$_2$ technology of electron beam (EB) with high energy (Zhu *et al.*, 2002). Although pulsed corona induced plasma chemical process (Masuda and Nakao, 1986), a more advanced technology than EB, is still under investigating in laboratory, many great achievements have been achieved in related areas, such as chemical reaction kinetics, gas phase electric discharge physics, nanosecond grade high voltage pulsed electric supply and pulsed corona reactor with the efforts of the scientists (Kim *et al.*, 2003; Ren *et al.*, 2004; Liu *et al.*, 2005; Yan *et al.*, 2006). A new technology derived from it, combining plasma with adsorption, has also been studied extensively and made great progress in the application. However, there are still some key theoretical and technological problems which should be resolved

before applying this technology to remove NO and SO$_2$ in power plant. Among them, how to reduce reaction energy-consumption and increase NO and SO$_2$ removal efficiency greatly may be very important and difficult.

In order to solve the above two problems, the following three aspects can be considered. (1) Many investigations have indicated that NO can be reduced to N$_2$ by active N atom (Penetrante *et al.*, 1999; Yu *et al.*, 2005a), and the by-product of this reaction is active O atom. Obviously, the active O atom from NO can react with SO$_2$ through some process, and this can not only utilize the energy of the active O atom, but also realize NO and SO$_2$ removal simultaneously. Thus, NO reduction may induce SO$_2$ oxidation sequentially. (2) When gas molecule (N$_2$) is absorbed on the surface of some suitable dielectric absorbent pellets, N–N bond will be elongated, and this will reduce the energy used to ionize the gas molecule (N$_2$). Then, the energy-consumption used to reduce NO will also be reduced. (3) We suppose that the sequential removal process in (1) can go on the surfaces of some suitable dielectric absorbent pellets in (2), then the sequential removal efficiency can be further improved if such dielectric absorbent pellet can be manufactured, it can selectively absorb those contributing gas molecules (N$_2$, NO and SO$_2$) in the sequential plasma reaction, while absorb in the least amount those counteractive gas molecules (O$_2$).

The above explanation indicated that the sequential

removal of NO and SO$_2$ using non-thermal plasma and adsorbent simultaneously may be a possible process with low energy-consumption and high removal efficiency.

In this sequential removal process, there are very little O$_2$ and H$_2$O vapor on the surface of the absorbent pellets. So, before intensively investigating this sequential removal process with low energy-consumption and high removal efficiency, the removal of NO and SO$_2$ from dry gas stream with very little O$_2$ using non-thermal plasma can be used to investigate the feasibility of the sequential removal process using non-thermal plasma and adsorbent simultaneously.

In this study, the removal of NO and SO$_2$ from dry gas stream (NO/SO$_2$/N$_2$/O$_2$; O$_2$ concentration is low) using non-thermal plasma was experimentally investigated using a coaxial dielectric barrier discharge. The experiments were carried out in the dry gas stream with and without Ar respectively at the O$_2$ concentration of 0.1%. The mechanism of De-SO$_2$ and De-NO in the dry gas stream was discussed and the possible way of improving the removal efficiency was pointed out.

# 1 Experimental system and methods

An experimental system shown in Fig.1 was established to study the removal of NO and SO$_2$ using non-thermal plasma. All the experiments were carried out at room temperature and normal atmospheric pressure.

## 1.1 Experimental system

The purities of NO and SO$_2$ were all 99.0% and the rest was N$_2$. The purity of N$_2$ was 99.9% and the rest was O$_2$. The purity of Ar is 99.9% and the rest was O$_2$. All the above gases were provided by Nanjing Special Gases Factory Cooperation Limited in China.

Pulsed electric supply with the model HB708 was provided by Foshan Nanhai Hongba Electronic Cooperation Limited in China. As presented in Fig.2, the output voltage reached as high as 10 kV, the frequency output was 30 kHz
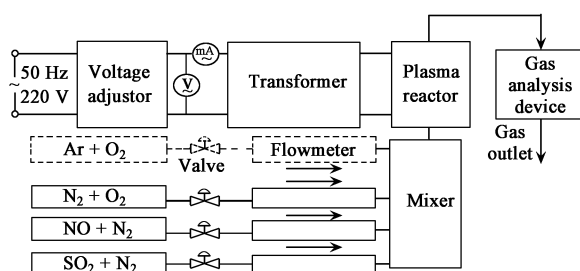


Fig. 1 Schematic system for NO and SO$_2$ removal with plasma.
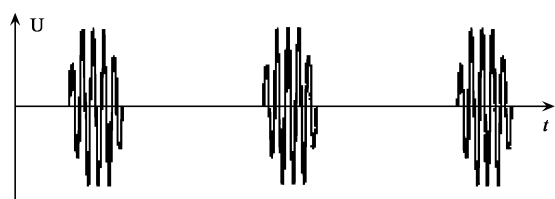


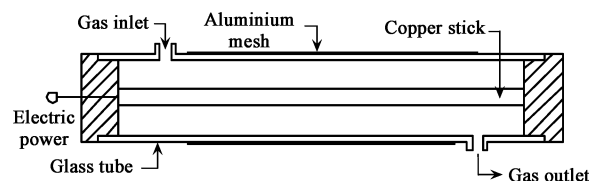Fig. 2 Wave shape of the pulsed voltage.



Fig. 3 Structure of plasma reactor.

and the duration of oscillation was 220 ns. The voltage input was adjusted using a voltage adjustor.

The plasma reactor in Fig.3 was a glass cylinder with a bronze rod as the inner electrode (diameter 8 mm). The glass cylinder was covered with a layer of aluminium mesh as the outer electrode, through which the discharge in the reactor could be looked into. The length of the aluminium mesh was 30 mm and the inner diameter of the glass cylinder is 15 mm.

A gas analyzer (Testo 360, Testo AG, Germany) was used to measure the concentration of each gas component before and after discharge.

## 1.2 Experimental procedures and methods

The experiments are divided into two parts: (1) N$_2$ was connected with a big flowmeter with flow rate unit of L/min, and NO and SO$_2$ gases were connected respectively with two small flowmeters with flow rate unit of ml/min. All the above flowmeters are provided by Changzhou Shuanghuan Thermo-Technical Instrument Cooperation Limited in China. The flowmeter of Ar will be turned off and the gas in the mixer will be the mixture of NO, SO$_2$, N$_2$ and O$_2$. The concentrations of NO and SO$_2$ will be adjusted respectively to two fixed values and then the laws of the removal efficiencies of NO and SO$_2$ varying with the voltage input of transformer can be obtained respectively. (2) Ar will be connected with the big flowmeter, and N$_2$, NO and SO$_2$ will be connected respectively with three small flowmeters. The flowmeter of Ar will be turned on and the gas in the mixer will be the mixture of NO, SO$_2$, Ar, N$_2$ and O$_2$. The concentrations of NO and SO$_2$ will be adjusted respectively to two fixed values and then the laws of the removal efficiencies of NO and SO$_2$ varying with the voltage input of the transformer can be obtained. Obviously, in the above two parts, O$_2$ concentrations are very small (0.1%) all the time. Because NO reduction efficiency is quite sensitive to the residence time (Yu *et al.*, 2005a) of the gas stream, the flux was controlled below 5 L/min so that there would be sufficient time for the reactions.

# 2 Results and discussion

The following analyses are on the basis of the experimental results of the removal of NO and SO$_2$ in the dry gas streams using non-thermal plasma. The main experiments were carried out in the dry gas stream with and without Ar respectively, and O$_2$ concentration was 0.1%.

The removal efficiencies of NO and SO$_2$ ($\eta_{NO}$, $\eta_{SO_2}$) are defined as the follows ($C_{NO}$ and $C_{SO_2}$ represent the

concentration of NO and SO$_2$ respectively):

$$\eta_{NO} = (C_{NO}^0 - C_{NO})/C_{NO}^0 \times 100\% \tag{1}$$

$$\eta_{SO_2} = (C_{SO_2}^0 - C_{SO_2})/C_{SO_2}^0 \times 100\% \tag{2}$$

where, $C_{NO}^0$ is NO concentration before discharge and $C_{NO}$ is NO concentration after discharge, $C_{SO_2}^0$ is SO$_2$ concentration before discharge and $C_{SO_2}$ is SO$_2$ concentration after discharge.

Figure 4 shows the change of the NO$_2$ concentration varies with the voltage input of the transformer under two different conditions (with and without Ar). Fig.5 shows NO and SO$_2$ removal efficiency varied with the voltage input of the transformer under two different conditions (with and without Ar). In all the above experiments, the initial concentrations of NO, SO$_2$, O$_2$ and NO$_2$ (NO$_2$ is produced by the reaction of NO and O$_2$) were $567 \times 10^{-6}$, $723 \times 10^{-6}$, $1000 \times 10^{-6}$ (0.1%) and $20 \times 10^{-6}$, respectively. In the experiments with Ar, N$_2$ was connected with the small flowmeter. So, the concentrations of N$_2$, NO, SO$_2$ and O$_2$ are all very small and at the same grade of magnitude, and this can help us to investigate the competitive abilities of active N atom and active O atom in removing NO molecule when O$_2$ concentration is very small.

From Fig.4 and Fig.5a, we can see that NO$_2$ concentration is almost at the same level all the time and the removal efficiency of NO is high, which indicate that the oxidation reaction between the active O atom and NO molecule can be ignored when the initial concentration of O$_2$ is very small (0.1%). So, NO removal mainly depends
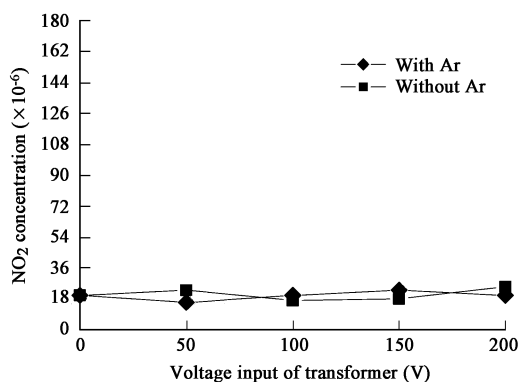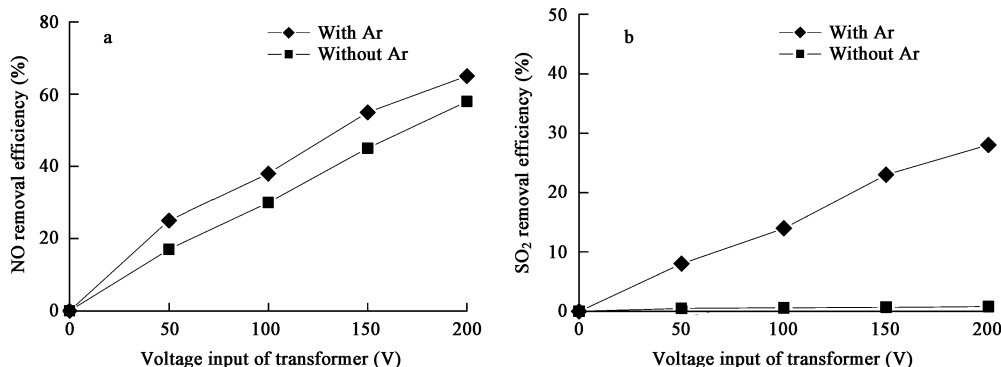
on the reduction reaction between the active N atom and NO molecule when O$_2$ concentration is very small, and the mechanism of the NO reduction reaction is as follows (Penetrante *et al.*, 1999; Yu *et al.*, 2005b):

$$e + N_2 \longrightarrow 2N + e \tag{3}$$

$$N + NO \longrightarrow N_2 + O \tag{4}$$

From Fig.5b, we can see that SO$_2$ removal efficiency is so small that it can be ignored when there is no Ar in the dry gas stream. This is consistent with the investigation results of Chang *et al.* (1991, 1992), which showed that SO$_2$ removal efficiency was so small that it could be ignored in the dry gas stream without H$_2$O vapor. Chang believed that SO$_3$ could react with active O atom and produce SO$_2$, and this reaction was so fast that the oxidation reaction between the active O atom and SO$_2$ molecule could not be observed. This fast reaction equation is (Westenberg and deHaas, 1975; Singleton and Cvetanovic, 1988):

$$O + SO_3 + M \longrightarrow SO_2 + O_2 + M \tag{5}$$
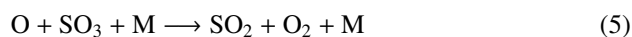
In Eq. (5), M refers to either N$_2$, O$_2$ or other gas molecular.

Also from Fig.5b, we can see that SO$_2$ removal efficiency can not be ignored when there is Ar in the dry gas stream and it seems that this is consistent with the investigation results of Sardja and Dhali (1990). They investigated SO$_2$ removal in the dry gas stream with N$_2$ and O$_2$, when the initial concentration of SO$_2$ was between $1000\times10^{-6}$ and $5000\times10^{-6}$ and the peak voltage of pulsed electric supply was 24 kV. The experimental results showed that SO$_2$ removal efficiency could reach as high as 50% and they believed that SO$_2$ was removed mainly through the following oxidation reaction between active O atom and SO$_2$ molecule:

$$O + SO_2 + M \longrightarrow SO_3 + M \tag{6}$$

In Eq. (6), M refers to either N$_2$, O$_2$ or other gas molecular.

For those gas streams with H$_2$O vapor, it is no doubt that H$_2$O plays an important role in oxidizing SO$_2$ (Sun *et al.*, 1996; Chang *et al.*, 1991, 1992) and SO$_2$ removal efficiency is high. But, for the above dry gas streams without H$_2$O vapor, Sardja and Dhali (1990) and Chang *et al.*



Fig. 4 NO$_2$ concentration vs. the voltage input of transformer with and without Ar.



Fig. 5  NO (a) and SO$_2$ (b) removal efficiency vs. the voltage input of transformer with and without Ar.

(1991, 1992) have obtained the above two conflicting $SO_2$ removal efficiencies and mechanisms, respectively. Our experimental results in Fig.5b also show the complexity of $SO_2$ removal when the gas stream is dry. So, from the above, we can see that the mechanism of $SO_2$ removal in the dry gas stream still need more detailed investigations.

The following is the discussion on the mechanism of $SO_2$ removal in the dry gas stream.

Dong *et al*. (2005) measured the spectrum of dielectric barrier discharge at atmospheric pressure using the special setup with two water electrodes and investigated the variation of spectrum when a little Ar was mixed. $N_2$ molecular spectrum and N atomic spectrum were found in the range of 300–800 nm. After a little Ar was mixed, the breakdown voltage of discharge obviously decreased. The spectral line intensities of $N_2$ molecules and N atoms increased. The full width at half maximum of spectral line was obviously broadened. Because Stark broadening is a linear function of electron density, it can be seen that electron density increased after a little Ar was mixed with the air, which caused the probability of excitation collision of $N_2$ and N with electrons to increase, and the number of $N_2$ and N excited to higher excitation state to increase. So the intensity of spectrum was intensified.

Using the gas mixture of $SO_2$ and $N_2$ and nanosecond grade high voltage pulsed electric supply, Wang *et al*. (1999) measured the weak emission spectrum of SO fragment produced by the positive corona discharge of $SO_2$ at room temperature and normal atmospheric pressure. Combining with related analyzing, one of the reasons why the emission spectrum was weak was found to be the small electron density in the plasma and the mechanism of $SO_2$ removal was analyzed. The electrons and other species collide with $SO_2$ and $SO_2$ is broken into SO fragment. Then SO fragment reacts easily with $O_2$ and produces $SO_3$ through the following reaction:

$$SO + O_2 \longrightarrow SO_3 \qquad (7)$$

Or when SO failed to react with $O_2$, S–O bond may be collided by the species in the plasma and broken into S.

According to our experimental results, combining the above investigation results of Dong *et al*. (2005) and Wang *et al*. (1999), we can deduced the mechanism of $SO_2$ removal in the dry gas stream as follows: when there is no Ar in the dry gas stream, the electron density will be very small and this can cause few SO fragments produced, so little $SO_2$ can be removed through the reaction between SO and $O_2$ or breaking of S–O bond and $SO_2$ removal can be ignored; while the electron density will be increased greatly when there is Ar in the dry gas stream and this can cause much more SO fragments produced, so much more $SO_2$ is removed through the reaction between SO and $O_2$ or breaking of S–O bond and $SO_2$ removal efficiency is much high. This is also the reason of the difference of NO removal efficiency with Ar and without Ar in Fig.5a. From Fig.5a, we can see that NO removal efficiency of the dry gas stream with Ar is higher than that of the dry gas stream without Ar.

From the above analyses, the reason of the two investi-gation results of Sardja and Dhali (1990) and Chang *et al*. (1991, 1992) are conflicting is just because the electron densities in two reactor are different. The high electron density in the reactor used by Sardja and Dhali caused high $SO_2$ removal efficiency and their experimental results are not conflicting actually. So, the electron density of plasma is very important to $SO_2$ removal and adopting some methods to increase the electron density in plasma can remove more $SO_2$ in the dry gas stream.

## 3 Conclusions

When $O_2$ concentration is very small (0.1%), the com-parison experimental results of De-$SO_2$ and De-NO in the dry gas stream ($NO/SO_2/N_2/O_2$) using non-thermal plasma under two different conditions (with and without Ar) and related analyzing indicate that: NO is mainly converted to $N_2$ by active N atom when $O_2$ concentration is very small; Ar can cause much more active N atoms produced in the dry gas stream and these active N atoms can reduce much more NO molecules; $SO_2$ is mainly removed through the reaction between SO and $O_2$ or breaking of S–O bond; few SO fragments can be produced in the dry gas stream with-out Ar and $SO_2$ removal efficiency is so small that it can not be observed; Ar can cause more SO fragments produced and then $SO_2$ removal efficiency can be observed; some methods can be adopted to increase the electron density in plasma and then the removal efficiencies of NO and $SO_2$ will be increased.

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