Available online at www.sciencedirect.com
ScienceDirect
Journal of Environmental Sciences 21(2009) 328–332
JOURNAL OF ENVIRONMENTAL SCIENCES
ISSN 1001-0742
CN 11-2629/X
www.jesc.ac.cn

Simultaneous oxidation of NO, SO_2 and Hg^0 from flue gas by pulsed corona discharge

XU Fei, LUO Zhongyang*, CAO Wei, WANG Peng, WEI Bo, GAO Xiang, FANG Mengxiang, CEN Kefa

State key Laboratory of Clean Energy Utilization, Zhejiang University, Hangzhou 310027, China.
E-mail: feix@zju.edu.cn

Received 18 April 2008; revised 20 June 2008; accepted 15 July 2008

Abstract

A process capable of simultaneously oxidizing NO, SO_2, and Hg^0 was proposed, using a high-voltage and short-duration positive pulsed corona discharge. By focusing on NO, SO_2, and Hg^0 oxidation efficiencies, the influences of pulse peak voltage, pulse frequency, initial concentration, electrode number, residence time and water vapor addition were investigated. The results indicate that NO, SO_2 and Hg^0 oxidation efficiencies depend primarily on the radicals (OH, HO_2, O) and the active species (O_3, H_2O_2, etc.) produced by the pulsed corona discharge. The NO, SO_2 and Hg^0 oxidation efficiencies could be improved as pulse peak voltage, pulse frequency, electrode number and residence time increased, but they were reduced with increasing initial concentrations. By adding water vapor, the SO_2 oxidation efficiency was improved remarkably, while the NO oxidation efficiency decreased slightly. In our experiments, the simultaneous NO, SO_2, and Hg^0 oxidation efficiencies reached to 40%, 98%, and 55% with the initial concentrations 479 mg/m^3, 1040 mg/m^3, and 15.0 μg/m^3, respectively.

Key words: pulsed corona discharge; NO; SO_2; Hg^0; radical; active species; oxidation efficiency
DOI: 10.1016/S1001-0742(08)62272-X

Introduction

Various air pollutants are emitted into atmospheric from power plants. NO and SO_2 are the most abundant, which could cause acid rain. Besides, trace heavy metals are also considered as hazardous air pollutants, in which mercury is concerned most. Therefore, how to control NO, SO_2, and mercury emission from flue gas is becoming hotspot (Man *et al*., 2005; Wu *et al*., 1998; Streets *et al*., 2005). Up to now, wet flue gas desulfurization (WFGD) technology is still the most effective and widely used method for SO_2 removal (Cheng *et al*., 2003), and SCR is considered as the most effective method for NO_x reduction (Wendt *et al*., 2001). For mercury control, many technologies, including the injection of sorbets such as active carbon, were developed and investigated. However, the individual treatments result in expensive investment and operating cost. Researchers focused on developing new technology for simultaneous removal of NO, SO_2 and mercury from flue gas.

It is known that NO is insoluble in water and difficult to remove, in contrast NO_2 can react with water forming acid species which can be efficiently removed by WFGD. Mercury in the flue gas usually exists in the forms of elemental mercury (Hg^0) and oxidized mercury (Hg^{2+}), WFGD technology can remove nearly 90% of Hg^{2+} but none of Hg^0. Therefore, converting NO and Hg^0 to NO_2 and Hg^{2+} can control NO and mercury emission. As a result, pre-oxidation was put forward. PPCP, a new method for SO_2 removal in flue gas has been introduced and the fact that O, OH, O_3 radicals can efficiently oxidize NO to NO_2, Hg^0 to Hg^{2+} has been reported (Masuda *et al*., 1987; Onda *et al*., 1997; Wu *et al*., 2003). Therefore, it is possible for simultaneous removal of NO, SO_2 and mercury in one washing tower by pre-oxidation of NO, SO_2 and Hg^0.

Pulsed corona discharge is considered an effective method to oxidize the air pollutants (Liang *et al*., 2002; Wang *et al*., 2005; Ighigeanu *et al*., 2005). High-voltage and short-duration positive pulsed corona discharge have been found to generate high-energy electrons, which can efficiently dissociate, excite, and ionize N_2, O_2 and H_2O into reactive radicals (OH, HO_2, O, N, H, etc.) and active species (O_3, H_2O_2, etc.). These radicals and active species such as O, OH, HO_2, O_3 play important roles in NO, SO_2 and Hg^0 oxidation from combustion flue gas. This article presented the detailed investigations on the oxidation of NO, SO_2 and Hg^0 by pulsed corona discharge. A wire-plate electrode configuration was designed to investigate the effects of pulse peak voltage, pulse frequency, initial concentration, electrode number, residence time, and water vapor addition on oxidation efficiencies.

* Corresponding author. E-mail: zyluo@cmee.zju.edu.cn

1 Oxidation mechanisms

The process of simultaneous oxidation of NO, SO_2 and Hg^0 in flue gas is divided into two periods. The first period is the generation of oxygenated radicals and active species. During pulsed corona discharge, more electrical energy input goes into the production of energetic electrons than gas heating. High-energy electrons (the energy is in range of 5–20 eV) produced by pulsed corona discharge collide with the background molecules and efficiently dissociate, excite, and ionize N_2, O_2 and H_2O into oxygenated radicals and active species (Dong and Zhang, 2006; Wang *et al.*, 2006).

The second period is radicals and active species utilization for pollutants oxidation reaction. There were variety of complex chemical reactions occurred in the reactor (Mok and Nam, 2002; Wang *et al.*, 2007; Byun *et al.*, 2007). During this period, NO and SO_2 were oxidized to NO_2, SO_3 and corresponding acid mist; while Hg^0 is oxidized to Hg^{2+} by pulsed corona discharge.

2 Experimental setup and method

2.1 Experimental setup

The experimental setup is illustrated schematically in Fig. 1. It is mainly composed of a simulated flue gas generator, a pulsed corona discharge reactor, a pulse waveform measurement system, an on-line gas analysis system, and a tail gas treatment system.

The pulse power supply is of type NM0.75-60 (Sichuan Jiuhuan, China), which is designed to produce high voltage pulse with a rising time of about 300 ns, duration of about 500 ns and an adjustable repetition frequency of 7–300 Hz. The maximum pulse peak voltage is 60 kV and the mean output power is 500 W. The pulsed corona discharge voltage is measured with a 1000:1 high-voltage probe (P6015A, Tektronix, USA) and a digital oscilloscope (TDS3034B, Tektronix, USA). Four sample waveforms for the positive pulses of different peak voltages (25, 38, 48, and 53 kV) are shown in Fig. 2.

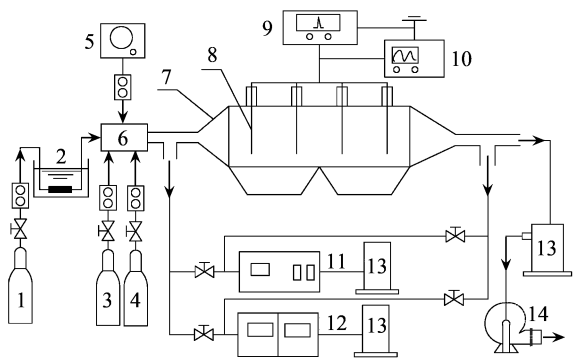

Fig. 1 Experimental setup for simultaneous oxidation of NO, SO_2, and Hg^0. (1) N_2; (2) Hg^0; (3) SO_2; (4) NO; (5) water vapor addition; (6) mixing tank; (7) reactor; (8) electrode; (9) pulse power supply; (10) oscilloscope; (11) gas analyzer; (12) mercury analyzer; (13) tail gas treatment; (14) exhauster.

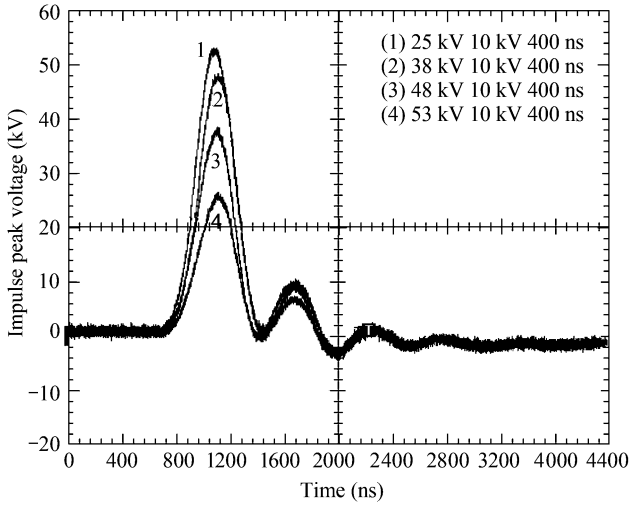

Fig. 2 Oscillogram of positive impulse with different peak voltages.

A detailed drawing of the pulsed corona discharge reactor is illustrated in Fig. 3. The reactor is of wire-plate structure, which mainly consists of two polished stainless steel plates as the cathodes and four line discharge electrodes in middle as the anodes. The diameter of the discharging wire is 1.0 mm with an effective discharge length of 200 mm. The distance between wire and plate is 60 mm, and the wires are placed at intervals of 100 mm. The two plates are grounded. The pulsed corona discharge is induced by the application of fast-rising narrow positive high voltage pulse to the wire-plate geometry. It develops by forming a number of streamers, the starting points of which are distributed over the surface of discharging wires (Mok and Nam, 2002). The concentrations of NO and SO_2 were measured using a gas analyzer (NGA2000, Rosemount, Germany); and the concentrations of Hg^0 and Hg^{2+} were measured with MS-1A/DM-6A (Nippon Instrument Corporation, Japan).

2.2 Experimental method

To obtain the oxidation efficiencies, the initial concentrations of NO, SO_2 and Hg^0 at the reactor inlet and their concentrations at the reactor outlet were measured respectively, before and after the pulsed corona discharge applied to the discharge electrodes. In this study, the mean concentrations in 2 min were determined for oxidation

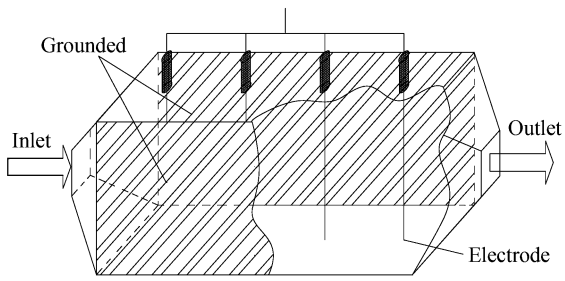

Fig. 3 Schematic diagram of pulsed corona discharge reactor.

efficiencies calculation by Eqs. (1)–(3).

$$\eta_{NO} = \frac{C_{NO\text{-inlet}} - C_{NO\text{-outlet}}}{C_{NO\text{-outlet}}} \times 100\% \quad (1)$$

$$\eta_{SO_2} = \frac{C_{SO_2\text{-inlet}} - C_{SO_2\text{-outlet}}}{C_{SO_2\text{-inlet}}} \times 100\% \quad (2)$$

$$\eta_{Hg^0} = \frac{C_{Hg^0\text{-inlet}} - C_{Hg^0\text{-outlet}}}{C_{Hg^0\text{-inlet}}} \times 100\% \quad (3)$$

where, $C_{NO\text{-inlet}}$, $C_{SO_2\text{-inlet}}$ and $C_{Hg^0\text{-inlet}}$, and $C_{NO\text{-outlet}}$, $C_{SO_2\text{-outlet}}$ and $C_{Hg^0\text{-outlet}}$ are the concentrations of NO, SO_2 and Hg^0 at the reactor inlet and outlet, respectively.

3 Results and discussion

3.1 Effects of pulse peak voltage and frequency on NO, SO_2, Hg^0 oxidation efficiency

The initial NO, SO_2 and Hg^0 concentrations were kept at 479 mg/m^3, 1040 mg/m^3, and 23.1 μg/m^3, respectively, with 4 discharge electrodes and residence time 6 s. The water vapor volume ratio was set at 1%. The experimental pulse peak voltages were 25, 38, 48, and 53 kV, and the pulse frequency were controlled at 50, 100, 150, 200, 250, and 300 Hz.

As shown in Fig. 4a, at lowest peak voltage 25 kV, NO and SO_2 oxidation efficiencies are only about 10%, but they increase rapidly with the increasing of peak voltage, especially for SO_2. The oxidation efficiency of SO_2 can reach near 80% at the highest peak voltage 53 kV. This effect could be explained by that the electric-field intensity increases at the higher peak voltage, and the corona discharge ability is strengthened. Hence, the amount of radicals (OH, HO_2, O) and active species (O_3, H_2O_2, etc.) increases as well. Because the oxidation efficiencies of NO, SO_2 and Hg^0 depend primarily on the radicals and active species. As a result, the oxidation efficiencies are enhanced at a high peak voltage, and could reach to the maximum value at a voltage which is just lower the sparking discharge voltage.

As shown in Fig. 4b, the oxidation efficiencies are increased almost linearly with an increasing of pulse frequency. One possible explanation for this phenomenon is that with high pulse frequency, the input power in unit time are increased and the production of those radicals and active species are correspondingly increased. Hence, the collision probability of radicals and active species with pollutants such as NO, SO_2, Hg^0 are increased, thus enhancing the oxidation efficiencies. In this study, at 53 kV and 300 Hz, the NO, SO_2, and Hg^0 oxidation efficiencies reach about 43%, 80%, and 51%, respectively. Therefore, to improve the oxidation efficiencies, a high pulse frequency and the critical voltage which is just under the sparking discharge voltage are favorable.

3.2 Effect of initial concentration on NO, SO_2, Hg^0 oxidation efficiency

The following experiments were performed at 53 kV and 300 Hz, with 4 discharge electrodes and residence time 6 s, the water vapor volume ratio 1%. The initial NO concentrations were 131, 197, 344, 479, and 599 mg/m^3. The initial SO_2 concentrations were 300, 586, 1040, 1177, and 1494 mg/m^3. The initial Hg^0 concentrations were 4.6, 8.9, 15.0, 23.1, and 28.7 μg/m^3.

The NO, SO_2, and Hg^0 oxidation efficiencies were all reduced as the initial concentrations increase (Fig. 5). For NO, the oxidation efficiency drops from 90% to 20% when the initial concentration increases from 131 to 599 mg/m^3. For the highest initial SO_2 concentration (1494 mg/m^3), the oxidation efficiency is about 50%. When SO_2 concentrations were less than 600 mg/m^3, the oxidation efficiency can nearly reach to 100%. For Hg^0, the trend is quite similar. Because the number of high-energy electrons produced by pulsed corona discharges remained the same under the given conditions. When the initial NO, SO_2 and Hg^0 concentrations increase, there are more NO, SO_2 and Hg^0 molecules in the gas phase, thereby the radical and active species concentrations available for pollutants oxidation become relatively low. Hence, it results in insufficient oxidation for high concentration pollutants. In brief, the oxidation efficiencies are diminished when the initial concentrations are increased.

3.3 Effects of electrode number and residence time on NO, SO_2, Hg^0 oxidation efficiency

The effects of electrode number and residence time on NO, SO_2 and Hg^0 oxidation efficiency were investigated at

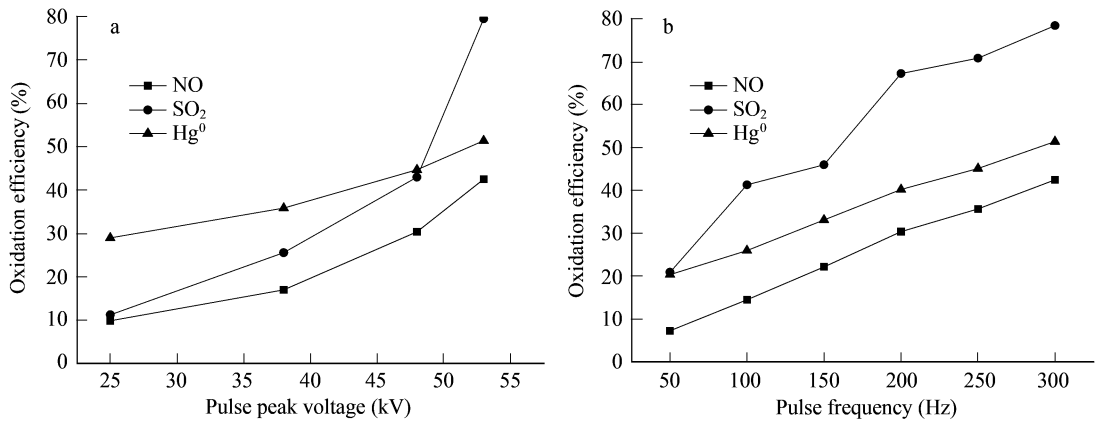

Fig. 4 Effects of pulse peak voltage (a) and frequency (b) on NO, SO_2 and Hg^0 oxidation efficiency.

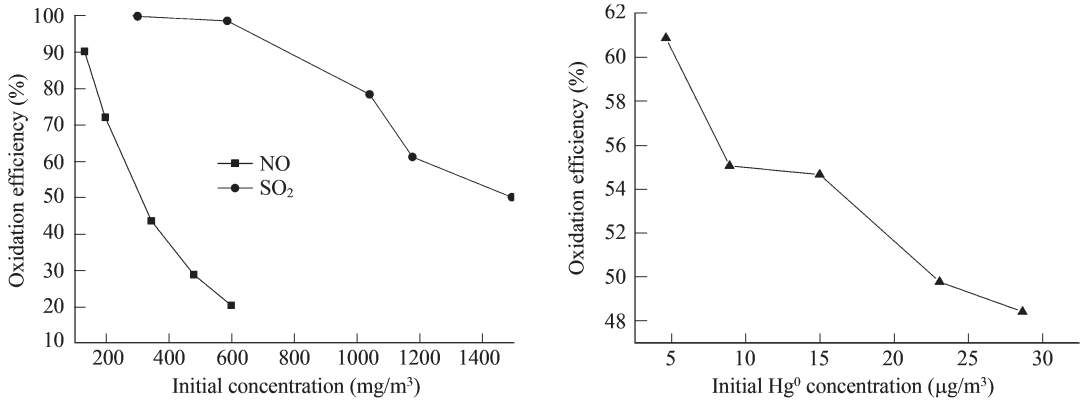

Fig. 5 Effect of initial concentration on NO, SO_2, and Hg^0 oxidation efficiency.

53 kV and 300 Hz, by changing the electrode number and residence time which obtained through varying flow rate. The initial NO, SO_2 and Hg^0 concentrations were kept at 479 mg/m^3, 1040 mg/m^3 and 15.0 μg/m^3, respectively. The water vapor volume ratio was set at 1%.

As shown in Fig. 6a, the oxidation efficiencies increase approximately linearly with increasing electrode number. We hypothesize that when the electrode number was increased, the length of pulsed corona discharge area was extended and more high-energy electrons were produced in the reactor, thus providing more chances for radical and active species formation. Hence, the collision probability between radicals and active species with pollutants is increased and the oxidation efficiency increased correspondingly. For the same number electrodes, SO_2 has the highest oxidation efficiency and NO has the lowest. From Fig. 6b, we find that the oxidation efficiencies are improved with an increase residence time, especially when the residence time is below 6 s. After that, the oxidation efficiencies increase slowly with the time prolonged. The results suggest that 6 s is the optimum residence time for oxidation process, where the oxidation reach to maximum.

3.4 Effect of water vapor addition on NO and SO_2 oxidation efficiency

Experiments have also been carried out to investigate the effect of water vapor addition on NO and SO_2 oxidation efficiency. The initial NO and SO_2 concentrations were kept at 479 and 1040 mg/m^3, respectively, with 4 discharge electrodes and residence time 6 s. The water vapor volume ratio increased from 1% to 2% with varying pulse peak voltage. The pulse frequency was kept at 300 Hz.

As shown in Fig. 7, with the water vapor addition, SO_2 oxidation efficiency was improved greatly. This observed phenomenon can possibly be explained as follows. As more H_2O molecules added into the reactor the SO_2 gas dissolved in water became easily and the production of OH and HO_2 radicals was enhanced. Those two comprehensive factors improve SO_2 oxidation efficiency eventually.

In contrast, NO oxidation efficiency was slightly decreased with water vapor addition. The reason was that with more water vapor addition, there are more H_2O molecules, which could capture large numbers of electrons and thus decrease the density of high-energy electrons (Wang *et al.*, 2005). It reduced the densities of O and O_3 radicals, which were considered to be important in NO oxidation. As a result, an increase in water vapor addition can reduce NO oxidation efficiency by pulsed corona discharge. It was also found that under the same conditions, the oxidation efficiencies increase with the increasing pulse peak voltage. The result agreed well with the experiments performed before.

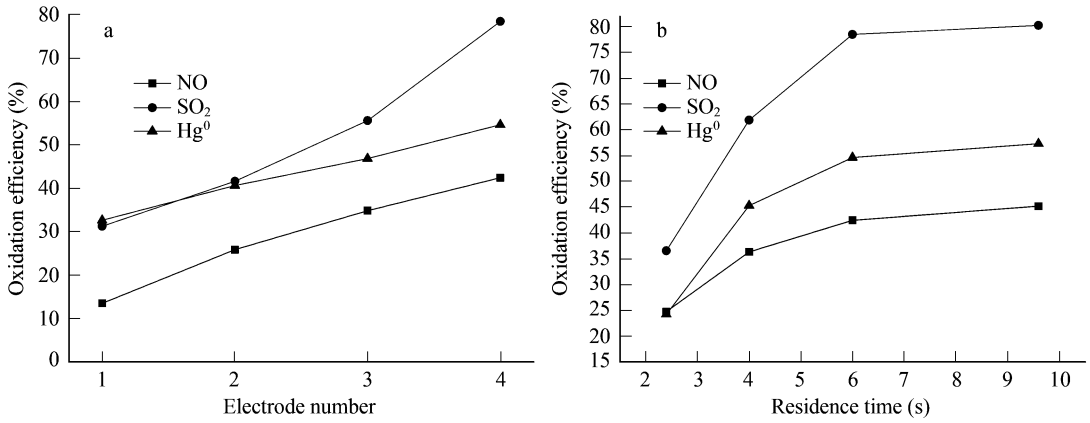

Fig. 6 Effects of electrode number (a) and residence time (b) on NO, SO_2 and Hg^0 oxidation efficiency.

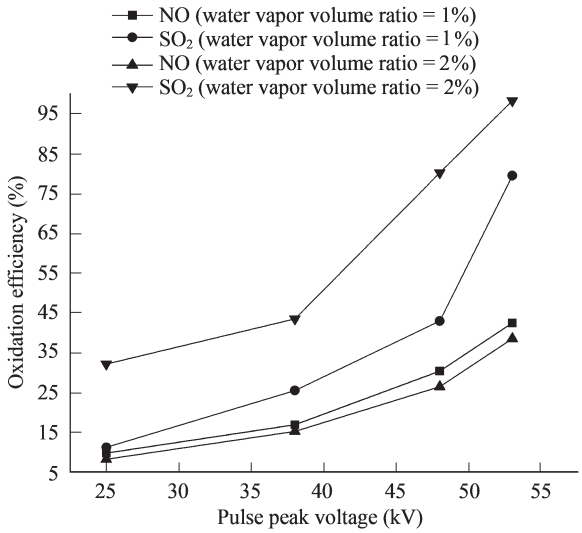

Fig. 7 Effect of water vapor addition on NO and SO_2 oxidation efficiency.

4 Conclusions

In this study, the simultaneous oxidations of NO, SO_2 and Hg^0 by positive pulsed corona discharge with wire-plate electrode at atmospheric pressure were successfully performed. Our results suggest that positive pulsed corona discharge had important implications for NO, SO_2 and Hg^0 oxidation, and the oxidation efficiencies are primarily dependent on the radicals (OH, HO_2, O) and the active species (O_3, H_2O_2), etc.

Acknowledgments

This work was supported by the Science and Technology Research of Department of Education of China (No. 0305, 03087).

References

Byun Y, Ko K B, Cho M H, Namkung W, Shin D N, Koh D J, Kim K T, 2007. Oxidation of elemental mercury using dielectric barrier discharge process. *Korean Chemical Engineering Research*, 45(2): 183–189.

Cheng J, Zhou J, Liu J Z, Zhou Z J, Huang Z Y, Cao X Y, Zhao X, Cen K F, 2003. Sulfur removal at high temperature during coal combustion in furnaces: a review. *Progress in Energy and Combustion Science*, 29: 381–405.

Dong B Y, Zhang D C, 2006. A review of pulsed discharge for SO_2 and NO_x removal from flue gas. *Techniques and Equipment for Environmental Pollution Control*, 7: 17–20.

Ighigeanu D, Martin D, Zissulescu E, Macarie R, Oproiu C, Cirstea E, Iovu H, Calinescu I, Iacob N, 2005. SO_2 and NO_x removal by electron beam and electrical discharge induced non-thermal plasma. *Vaccum*, 77: 493–500.

Liang X H, Looy P C, Jayaram S, 2002. Mercury and other trace elements removal characteristics of DC and pulse-energized electrostatic precipitator. *IEEE Transactions on Industry Applications*, 38: 69–76.

Man C K, Gibbins J R, Witkamp J G, Witkamp J, Zhang J, 2005. Coal characterization for NO_x prediction in air-staged combustion of pulverized coals. *Fuel*, 84: 2190–2195.

Masuda S, Wu Y, Urabe T, 1987. Pulse corona induced plasma chemical process for $DeNO_x$, $DeSO_x$ and mercury vapor control of combustion gas. Proc. 3rd. International Conference Electrostatic Precipitation, Abano, Italy. 667–676.

Mok Y S, Nam I S, 2002. Modeling of pulsed corona discharge process for the removal of nitric oxide and sulfur dioxide. *Chemical Engineering Journal*, 85: 87–97.

Onda K, Kasuga Y, Kato K, 1997. Electric discharge removal of SO_2 and NO_x from combustion flue gas by pulsed corona discharge. *Energy Conversion and Management*, 38: 1377–1387.

Streets D G, Hao J M, Wu Y, 2005. Anthropogenic mercury emissions in China. *Atmospheric Environment*, 39: 7789–7806.

Wang W C, Zhao Z B, Liu F, Wang S, 2005. Study of NO/NO_x removal from flue gas contained fly ash and water vapor by pulsed corona discharge. *Journal of Electrostatics*, 63: 155–164.

Wang W C, Wang S, Liu F, Zheng W, Wang D Z, 2005. Optical study of OH radical in a wire-plate pulsed corona discharge. *Spectrochimica Acta Part A*, 63: 477–482.

Wang Z H, Zhou J H, Zhu Y Q, Wen Z C, Liu J Z, Cen K F, 2007. Simultaneous removal of NO_x, SO_2 and Hg in nitrogen flow in a narrow reactor by zone injection: Experimental results. *Fuel Processing Technology*, 88: 817–823.

Wendt J O L, Linak W P, Groff P W, Srivastava R K, 2001. Hybrid SNCR/SCR technologies for NO_x control modeling and experiment. *AIChE Journal*, 47: 2603–2617.

Wu Y, Li J, Wang N H, Li G F, 2003. Industrial experiments on desulfurization of flue gases by pulsed corona induced plasma chemical process. *Journal of Electrostatics*, 57: 233–241.

Wu Y, Wang N H, Zhu Y M, Zhang Y B, 1998. SO_2 removal from industrial flue gases using pulsed corona discharge. *Journal of Electrostatics*, 44: 11–16.