Oxidation of gaseous elemental mercury in a high voltage discharge reactor

WANG Meiyan, ZHU Tianle*, LUO Hongjing, TANG Ping, LI Huan

School of Chemistry and Environment, Beihang University, Beijing 100191, China. E-mail: zhutl@buaa.edu.cn

Abstract

Effects of the voltage waveform, discharge tooth wheel number and $CO_2/NO/SO_2$ concentration in the simulated flue gas on Hg^0 oxidation were investigated using a link tooth wheel-cylinder reactor energized by different high voltage power supplies. Negative DC discharge induced more ozone production and a higher Hg^0 oxidation efficiency than positive DC discharge and 12 kHz AC discharge. The discharge tooth wheel number had almost no effect on the maximum Hg^0 oxidation efficiency. The allowable supplied voltage decreased with the increase of discharge tooth wheel number. CO_2 could stabilize the discharge process and increase the maximum voltage for a stable discharge. It has also been found that NO consumed O_3 induced by high voltage discharge, thereby decreased Hg^0 oxidation efficiency; while SO_2 had a slight promoting effect on Hg^0 oxidation.

Key words: plasma; Hg^0; flue gas; oxidation

DOI: 10.1016/S1001-0742(08)62469-9

Introduction

Mercury is a heavy metal considered detrimental to both humans and the ecosystem because of its high toxicity to the central nervous system and the tendency to bio-accumulate in human body. Lack of control of Hg emissions means huge environmental costs. A research showed that the remediation costs of Hg-contaminated sites, ranging between $2500 and 1.1 million per kg Hg isolated from the biosphere, is far higher than those of avoiding Hg pollution (Hylander *et al.*, 2006). Thus, prevention combined with control measures is cost-effective on a global basis.

Environmental mercury levels, however, have considerably heightened in recent years because of increasing mercury emissions. Global emissions of anthropogenic mercury to the atmosphere were estimated to be 1990 tons in 1995 (Pacyna and Pacyna, 2002), and rose to 2190 tons in 2000 (Pacyna *et al.*, 2006). According to the estimation of Pacyna *et al.* (2006), mercury emissions from anthropogenic activities in China reached more than 600 tons in 2000, about 28% of the global emissions of mercury. Based on the official energy consumption and material yield data, anthropogenic mercury emissions in China were estimated to be (536 ± 236) tons, and approximately 38% of the Hg came from coal combustion for year 1999 (Streets *et al.*, 2005).

Depending on the coal combustion conditions and flue gas chemistry, mercury compounds may be emitted as elemental mercury (Hg^0), oxidized mercury (Hg^{2+}), and particle-associated mercury (Hg_p). It is estimated that 56% of the Hg in China is released as Hg^0, 32% as Hg^{2+}, and 12% as Hg_p (Streets *et al.*, 2005). Of these, Hg^{2+} is much less volatile and more highly water-soluble than Hg^0, which makes it possible to employ wet scrubbing to control its emission. In addition, Hg_p can also be removed along with fly ash particles by using particulate control devices such as electrostatic precipitator (ESP) or fabric filter (Clack, 2006). In contrast to Hg^{2+} and Hg_p, Hg^0 is difficult to capture because it is volatile and insoluble in water (Pavlish *et al.*, 2003). Hence, developing novel mercury emission control technologies is required. On the whole, there are two broad approaches under development: (1) injecting sorbent to adsorb gaseous mercury and then enabling mercury removal by the conventional particulate control techniques; and (2) converting Hg^0 into Hg^{2+} species, which can be easily removed by the conventional wet scrubbing.

Activated carbon injection has been successfully applied for the control of mercury emissions from incineration. In order to improve mercury removal performance, many studies have been conducted regarding modification of activated carbon (Mei *et al.*, 2008; Lee *et al.*, 2004, 2006; Zeng *et al.*, 2004). The effectiveness of carbon injection technology to remove mercury in power plants, however, is not promising because of the low mercury concentration in flue gases. The high carbon-to-mercury weight ratios (3000:1–100000:1) and difficulties in sorbent regeneration result in an unacceptably high cost of using activated carbon as a sorbent (Granite *et al.*, 1999). Apart from extremely low mercury concentration, the factors that limit

the application of conventional mercury adsorption processes include speciation difference, short residence time, and high temperature. Thus, studies have been conducted to develop cost-effective alternatives to activated carbon (Lee et al., 2008).

Another trend in mercury removal from flue gas is converting Hg^0 into Hg^{2+} by non-thermal plasma. Many researchers have demonstrated that plasma-induced radicals can oxidize elemental mercury to the more easily treatable Hg^{2+} (Chen et al., 2006; Ko et al., 2008; Jeong and Jurng, 2007; Liang et al., 1998, 2002). Non-thermal plasma is widely considered to be a technically and economically feasible cleaning technique for the simultaneous removal of NOx and SO_2 (Chang et al., 2003; Yamamoto et al., 2002; Kuroki et al., 2002; Yan et al., 1998; Yan, 2001; Clements et al., 1989; He et al., 2007). It has also been reported that Powerspan Co. developed an electro-catalytic oxidation technology in which dielectric barrier discharge (DBD) plasma has been used to oxidize Hg^0, NOx, SO_2, and other trace elements, followed by wet ESP (McLarnon et al., 2000). To our knowledge, however, no systematic study on mercury oxidation by DC corona-induced plasma has been carried out so far.

In order to develop an integrated, cost-effective air pollution control technology for coal-fired power plants, our research group has been working on the simultaneous removal of SO_2, NO, Hg, and other pollutants from flue gas through the combination of non-thermal plasma and alkaline absorption. In this article, the influence of the operating parameters, as well as the concentrations of CO_2, NOx, and SO_2 in the simulated gaseous mixture on Hg^0 oxidation by non-thermal plasma induced by high voltage discharge were reported.

1 Materials and methods

1.1 Experimental setup

A schematic diagram of the experimental setup for this research work is shown in Fig. 1. It consists of a discharge reactor with a high voltage power supply, a gas feeding system, and a set of analytical instruments. Three types of high voltage power supplies, including positive/negative DC (input voltage: AC 220 V; output voltage: 0–25 kV) and 12 kHz AC (input voltage: AC 220 V; output peak-peak voltage: 0–25 kV), were used to investigate the influence of voltage waveform on Hg^0 oxidation. The discharge reactor used is similar to a wire-cylinder configuration, as shown in Fig. 2. The cylinder was a stainless steel tube (inner diameter 42 mm, length 400 mm), which served as ground electrode. The wire, acting as the active electrode, was a stainless tube with an outer diameter of 6 mm, on which twenty eight tooth wheels were strung at intervals of 10 mm equidistantly, except as otherwise mentioned. Four discharge points were evenly distributed on each tooth wheel.

1.2 Experimental method

Simulated flue gas was prepared using N_2, NO, SO_2, CO_2, air, and so on. Mass flow controllers were used to measure and control flow rates of dry gases from each cylinder. Water vapor was introduced to the gas mixture by passing the air through a temperature-controlled bubble tower containing water. Gaseous Hg^0 was added to the gas mixture from a temperature-controlled mercury vapor generator containing a mercury permeation tube.

All the experiments were conducted at atmospheric pressure, and the reaction temperature was kept at (80 ± 1) °C. The simulated flue gas with a total flow rate of 3 L/min, consisted of 6% O_2, 12% CO_2, 2.3% H_2O, and (110 ± 5) μg/m³ Hg using N_2 as balance gas, except as otherwise mentioned. The tubing used throughout the system was either stainless steel or Teflon to minimize the adsorption of gas composition on the inner wall. Heating tapes were used along the pipelines after the mercury generator and bubble tower to preheat the gas stream and prevent H_2O and Hg^0 condensation.

A flue gas analyzer (Testo 335, Germany) was used to monitor concentrations of SO_2, NO, NO_2, CO_2, and O_2. Ozone concentration was measured by indigo disulphonate
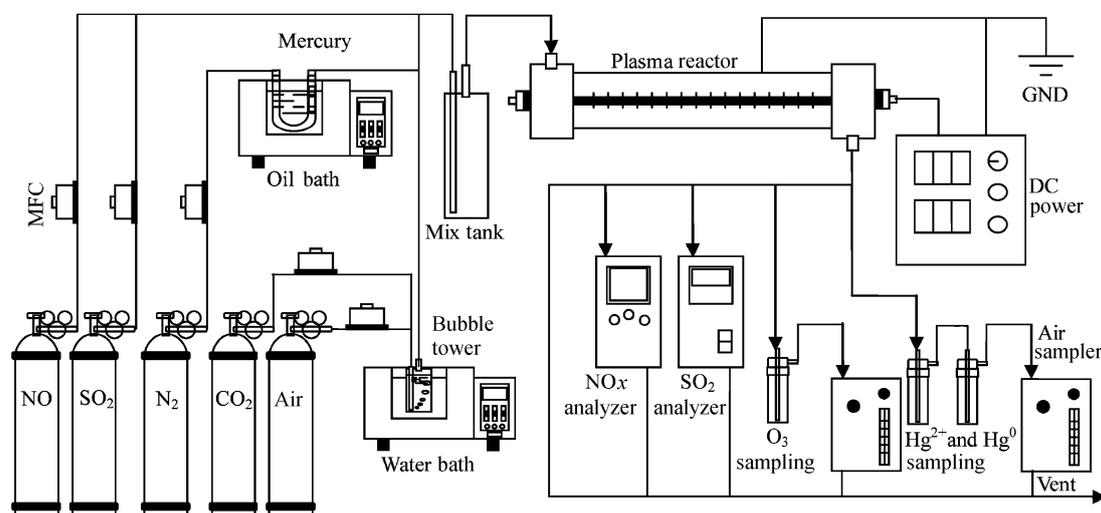

Fig. 1 Schematic diagram of the experimental setup.
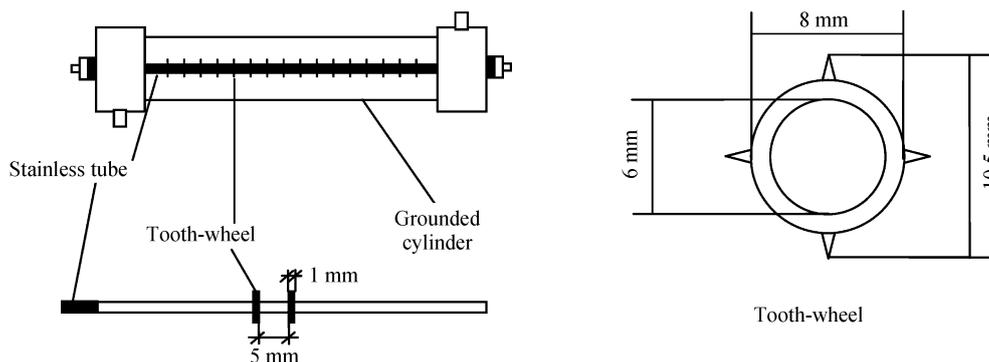
Fig. 2 Schematic diagram of discharge reactor.

spectrophotometry. Mercury was sampled only at the outlet of the plasma reactor and then analyzed by dithizone spectrophotometry. Oxidized mercury was absorbed by 0.5 mol/L sulfuric acid solution, and elemental mercury by a mixed solution of 0.1 mol/L potassium permanganate and 10% (*V/V*) sulfuric acid. The efficiency of Hg^0 conversion is hereby defined as:

$$\eta_{Hg^0} = \frac{C_{Hg^0_{off}} - C_{Hg^0_{on}}}{C_{Hg^0_{off}}} \times 100\% \qquad (1)$$

where, η_{Hg^0} (%) is Hg^0 oxidaiton efficiency. $C_{Hg_{on}}$ ($\mu g/m^3$) and $C_{Hg_{off}}$ ($\mu g/m^3$) are the concentrations of Hg^0 measured at the outlet of the plasma reactor with and without the corona discharge, respectively.

2 Results and discussion

2.1 Influence of voltage waveform on Hg^0 oxidation

The influence of voltage waveform on Hg^0 oxidation was studied using positive DC, negative DC, and 12 kHz AC. Figure 3a presents the Hg^0 oxidation efficiency as a function of supplied voltage for the three kinds of power supplies.

In present study, the supplied voltage initially increased from 0 to the highest voltage which maintained a stable discharge. Afterwards, Hg^0 oxidation was investigated from the highest voltage to the onset voltage. In Fig. 3a, it can be seen that the onset voltages of Hg^0 conversion were

9, 10, and 10 kV for negative DC, AC, and positive DC, respectively. In addition, Hg^0 oxidation was enhanced with increasing supplied voltage above the onset voltage, and the Hg^0 oxidation of negative DC was also much higher than those of positive DC and AC with the same supplied voltage. Figure 3a also indicates that the maximum voltages to maintain a stable discharge were different for the three kinds of power supplies, being 16, 14, and 13 kV corresponding to AC, negative DC and positive DC, respectively.

Various active radicals, such as OH·, O_3 and O·, were induced by electrons impacting with the gaseous components in the simulated flue gas when high voltage was applied between the active electrode and grounded electrode (Liang *et al.*, 1998). The reaction between these radicals and Hg^0 resulted in the oxidation of Hg^0 into Hg^{2+} (Calvert and Lindberg, 2005). Thus, the difference in the Hg^0 conversion may be attributed to the differences in the active species and their quantities induced by the different power supplies. The O_3 concentration of the discharge reactor outlet was also measured. It was noticed that the O_3 concentration for negative DC was significantly higher than those for positive DC and AC (Fig. 3b). Thus, it could be inferred that Hg^0 oxidation efficiency is proportional to O_3 concentration.

The above-mentioned results showed that the negative DC power supply had the optimal Hg^0 oxidation among the three kinds of power supplies. Hence, negative DC power supply was used in subsequent experiments.
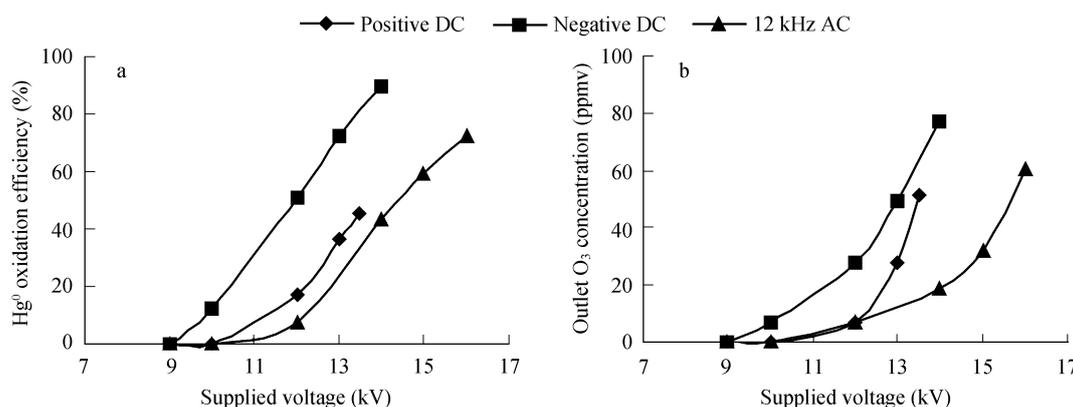

Fig. 3 Influence of voltage waveform on Hg^0 oxidation (a) and outlet O_3 concentration (b).

2.2 Influence of tooth wheel number on Hg^0 oxidation

The influence of tooth wheel number on Hg^0 conversion was investigated by changing the interval of the tooth wheels strung on the discharge electrode (Fig. 4). When the numbers of tooth wheels (*n*) were 7, 14 and 28, the corresponding intervals were 30, 20, and 10 mm, respectively.

It can be seen from Fig. 4 that an increased number of discharge tooth wheels results in a higher Hg^0 oxidation with the same supplied voltage. This can be attributed to the fact that specific injection energy is proportional to the number of tooth wheels. On the other hand, less discharge tooth wheel number leads to a higher available maximum supplied voltage. The maximum Hg^0 oxidation efficiency is almost the same for different tooth wheel numbers.

2.3 Influence of inlet CO_2 concentration on Hg^0 oxidation

The influence of inlet CO_2 concentration on Hg^0 oxidation was investigated in the presence of 6% O_2, 2.3% H_2O, and CO_2 with different inlet concentrations, using N_2 as balance gas (Fig. 5). As can be seen, the maximum voltages to maintain the stable discharge, corresponding to the inlet CO_2 concentration of 0, 6% and 12%, are 11, 12, and 14 kV, respectively. That is, the higher the inlet CO_2 concentration is, the higher the spark voltage is. It indicates clearly that CO_2 plays an important role in stabilizing the discharge process. Inlet CO_2 concentration, however, had almost no influence on the maximum Hg^0 oxidation efficiency.

2.4 Influence of inlet NO concentration on Hg^0 oxidation

The influence of inlet NO concentration on Hg^0 oxidation was first investigated in the absence of SO_2. In Fig. 6, we can see the Hg^0 oxidation as a function of the inlet NO concentration when the supplied voltage levels are 0 and 14 kV. Hg^0 oxidation did not occur and inlet NO concentration hardly had any influence on Hg^0 oxidation at 0 kV. When the supplied voltage was 14 kV, the presence of NO restrained Hg^0 oxidation, and Hg^0 oxidation efficiency decreased as the inlet NO concentration increased. The reason may be that Hg^0 oxidation relies on the radicals formed in the discharging process via the following reactions (Van
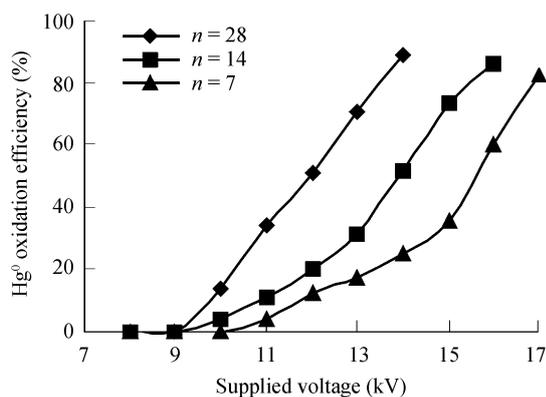
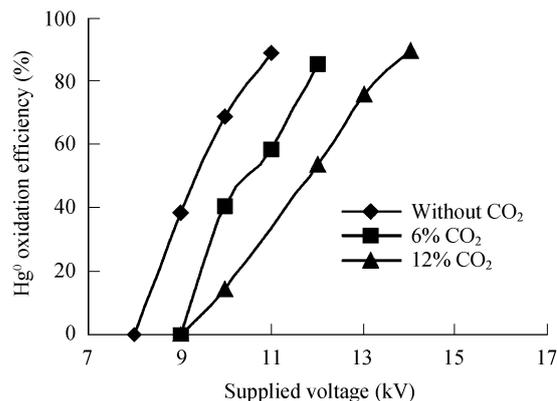**Fig. 4**   Influence of tooth wheel number on Hg^0 oxidation.

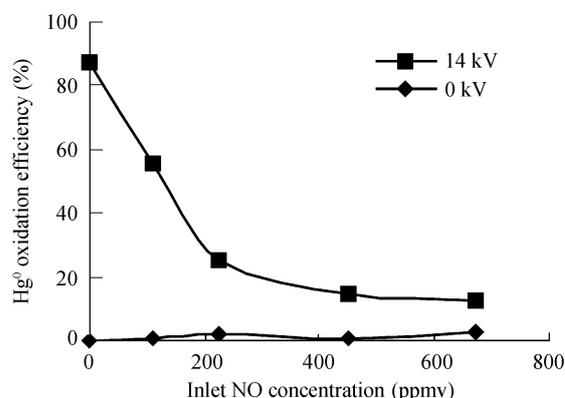**Fig. 5**   Influence of inlet CO_2 concentration on Hg^0 oxidation.

Fig. 6 Hg^0 oxidation efficiency as a function of inlet NO concentration.

Veldhuizen, 2000):

$$Hg + O \longrightarrow HgO \tag{2}$$

$$Hg + O_3 \longrightarrow HgO + O_2 \tag{3}$$

$$Hg + 2OH \longrightarrow Hg(OH)_2 \tag{4}$$
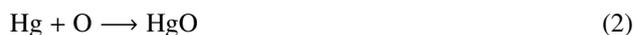
The presence of NO reduces the radicals to oxidize Hg^0 due to the consumption of these radicals by NO oxidation, as shown in the following reactions:

$$NO + O \longrightarrow NO_2 \tag{5}$$

$$NO + O_3 \longrightarrow NO_2 + O_2 \tag{6}$$

$$NO + OH \longrightarrow HNO_2 \tag{7}$$

$$NO_2 + OH \longrightarrow HNO_3 \tag{8}$$

In fact, the investigation of simultaneous outlet O_3 and NO concentrations also verified the above-mentioned statement. As shown in Fig. 7, the outlet O_3 concentration significantly decreased and NO_2 concentration dramatically increased with NO concentration increasing at 14 kV.

In this study, the influence of the inlet NO concentration on Hg^0 oxidation was also investigated in the presence of 175 ppmv SO_2. The results indicate that the relationships between Hg^0 oxidation efficiency, outlet O_3/NO_2 concentrations and the inlet NO concentration are similar to Figs. 6 and 7.
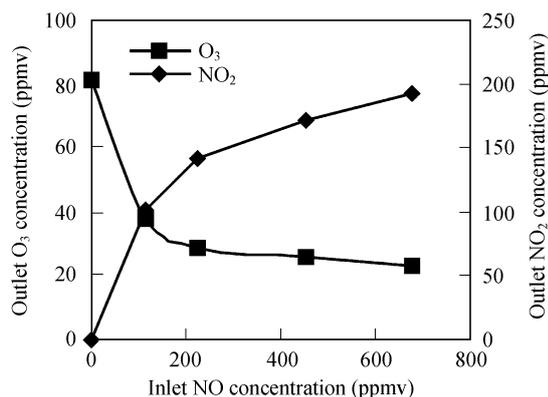
Fig. 7 Influence of inlet NO concentration on outlet O_3/NO_2 concentration at 14 kV.
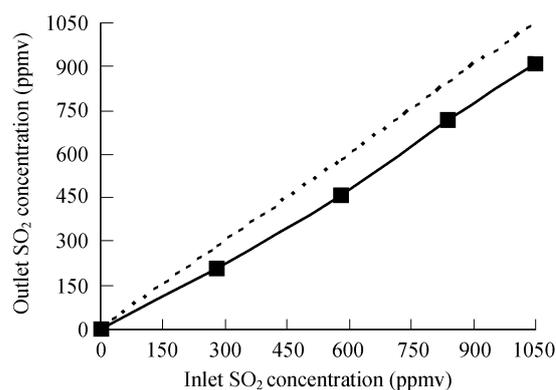

Fig. 9 Influence of inlet SO_2 concentration on outlet SO_2 concentration at 14 kV.
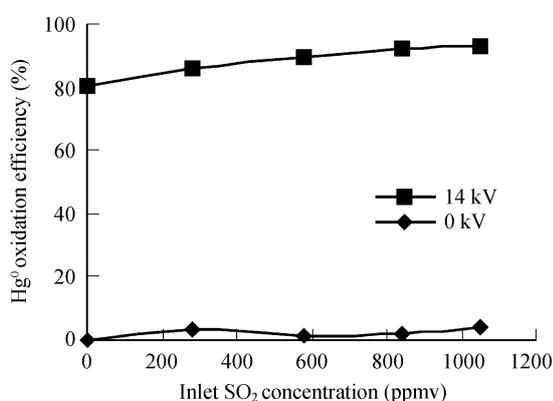

Fig. 8 Hg^0 oxidation efficiency as a function of inlet SO_2 concentration.
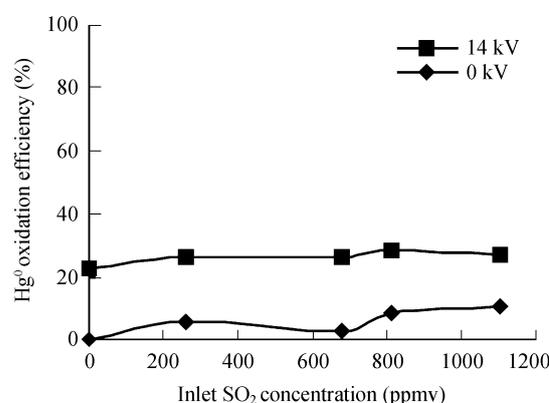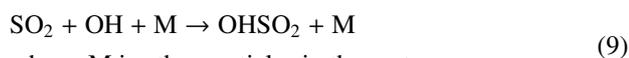

Fig. 10 Hg^0 oxidation as a function of inlet SO_2 concentration in the presence of NO.

2.5 Influence of inlet SO_2 concentration on Hg^0 oxidation

Figure 8 presents the Hg^0 oxidation efficiency as a function of inlet SO_2 concentration in the absence of NO, when the supplied voltage is 0 and 14 kV. Similar to the influence of inlet NO concentration, the Hg^0 oxidation did not occur at 0 kV even if the inlet SO_2 concentration increased from 0 to 1050 ppmv. The Hg^0 oxidation efficiency, however, slightly increased as the inlet SO_2 concentration increased at 14 kV.

A small quantity of SO_2 can be oxidized to SO_3 in the presence of active radicals induced by discharge. As a result, the outlet SO_2 concentration was lower than the inlet SO_2 concentration at 14 kV (Fig. 9). In addition, oxidized mercury is likely to react with SO_3 to form $HgSO_4$ (Van Veldhuizen, 2000). The following reactions are proposed to occur in the discharge reactor:

$$SO_2 + OH + M \rightarrow OHSO_2 + M \tag{9}$$

where, M is other particles in the system.

$$OHSO_2 + O_2 \longrightarrow SO_3 + HO_2 \tag{10}$$

$$HgO + SO_3 \longrightarrow HgSO_4 \tag{11}$$

The influence of inlet SO_2 concentration on Hg^0 oxidation was also investigated in the presence of 240 ppmv NO. Figure 10 shows that the influence of inlet SO_2 concentration on Hg^0 oxidation is slight in the presence of

NO. The inlet NO concentration had a dominant influence on Hg^0 oxidation.

3 Conclusions

The effects of operating parameters and gaseous compositions on Hg^0 oxidation were investigated in a discharge reactor. The following principal conclusions can be deduced from current work:

(1) Active radicals induced by high voltage discharge can oxidize elemental mercury. The Hg^0 oxidation efficiency increased with the increase of supplied voltage, and negative DC discharge obtained a higher Hg^0 oxidation efficiency than the positive DC discharge and 12 kHz AC discharge.

(2) As the discharge tooth wheel number increasing, supplied voltage corresponding to same Hg^0 oxidation efficiency decreased, while the maximum Hg^0 oxidation efficiency was almost unchanged.

(3) CO_2 in the simulated flue gas played an important role in stabilizing the discharge process. The highest voltage to maintain a stable discharge was enhanced with the increase of CO_2 concentration.

(4) The presence of NO resulted in a significant decrease of Hg^0 oxidation efficiency, while the promotion effect of SO_2 was very slight. Moreover, NO had a dominant effect

on Hg^0 oxidation when the reaction gas contained both NO and SO_2.

Acknowledgments

References

Calvert J G, Lindberg S E, 2005. Mechanism of mercury removal by O_3 and OH in the atmosphere. *Atmosphere Environment*, 39(18): 3355–3367.

Chang J S, Urashima K, Tong Y X, Liu W P, Wei H Y, Yang F M, 2003. Simultaneous removal of NOx and SO_2 from coal boiler flue gases by DC corona discharge ammonia radical shower systems: pilot plant tests. *Journal of Electrostatics*, 57(3-4): 313–323.

Chen Z Y, Mannava D P, Mathur V K, 2006. Mercury oxidization in dielectric barrier discharge plasma system. *Industrial and Engineering Chemistry Research*, 45(17): 6050–6055.

Clack H L, 2006. Mass transfer within electrostatic precipitators: in-flight adsorption of mercury by charged suspended particulates. *Environmental Science and Technology*, 40(11): 3617–3622.

Clements J S, Mizuno A, Finney W C, Davis R H, 1989. Combined removal of SO_2, NOx, and fly ash from simulated flue gas using pulsed streamer corona. *IEEE Transactions on Industry Applications*, 25(1): 62–69.

Granite E J, Pennline H W, Hargis R A, 1999. Carbons-based sorbents for the removal of mercury from flue gas. In: National Energy Technology Laboratory 1999 Conference on Unburn Carbon in Flyash: Processing and Utilization of High-LOI Flyash. Pittsburgh, PA. May 18.

He W, Zhu T L, Li J, 2007. NO conversion by positive streamer discharge – effects of gas compositions and reaction conditions. *Frontiers of Environmental Science and Engineering in China*, 1(2): 153–158.

Hylander L D, Goodsite M E, 2006. Environmental costs of mercury pollution. *Science of the Total Environment*, 368(1): 352–370.

Jeong J, Jurng J, 2007. Removal of gaseous elemental mercury by dielectric barrier discharge. *Chemosphere*, 68(10): 2007–2010.

Ko K B, Byun Y, Cho M, Namkung W, Shin D N, Koh D J, 2008. Influence of HCl on oxidation of gaseous elemental mercury by dielectric barrier discharge process. *Chemosphere*, 71(9): 1674–1682.

Kuroki T, Takahashi M, Okubo M, Yamamoto T, 2002. Single-stage plasma-chemical process for particulates, NOx, and SOx simultaneous removal. *IEEE Transactions on Industry Applications*, 38(5): 1204–1209.

Lee S F, Seo Y C, Jurng J, Lee T G, 2004. Removal of gas-phase elemental mercury by iodine- and chlorine-impregnated activated carbons. *Atmosphere Environment*, 38(29): 4887–4893.

Lee S H, Rhim Y J, Cho S P, Baek J I, 2006. Carbon-based novel sorbent for removing gas-phase mercury. *Fuel*, 85(2): 219–226.

Lee S S, Lee J Y, Keener T C, 2008. Novel sorbents for mercury emissions control from coal-fired power plants. *Journal of the Chinese Institute of Chemical Engineers*, 39(2): 137–142.

Liang X, Jayaram P, Looy P, Berezin A, Chang J S, 1998. Pulse corona application for the collection of mercury from flue gas. In: IEEE International Symposium on Electrial Insulation. Arlington, VA. June 7–10.

Liang X H, Looy P C, Jayaram S, Berezin A A, Mozes M S, Chang J S, 2002. Mercury and other trace elements removal characteristics of DC and pulse-energized electrostatic precipitator. *IEEE Transactions on Industry Applications*, 38(1): 69–75.

McLarnon C R, Horvath M L, Boyle P D, 2000. Electro-catalytic oxidation technology applied to mercury and trace elements removal from flue gas. In: Proceedings of the Air Quality II: Mercury, Trace Elements, and Particulate Matter Conference. McLean, VA. September 19–21.

Mei Z J, Shen Z M, Zhao Q J, Wang W H, Zhang Y J, 2008. Removal and recovery of gas-phase element mercury by metal oxide-loaded activated carbon. *Journal of Hazardous Materials*, 152 (2): 721–729.

Pacyna E G, Pacyna J M, 2002. Global emission of mercury from anthropogenic sources in 1995. *Water, Air, and Soil Pollution*, 137(1-4): 149–165.

Pacyna E G, Pacyna J M, Steenhuisen F, Wilson S, 2006. Global anthropogenic mercury emission inventory for 2000. *Atmosphere Environment*, 40(22): 4048–4063.

Pavlish J H, Sondreal E A, Mann M D, Olson E S, Galbreath K C, Laudal D L, 2003. Status review of mercury control options for coal-fired power plants. *Fuel Processing Technology*, 82(2-3): 89–165.

Streets D G, Hao J M, Wu Y, Jiang J K, Chan M, Tian H Z *et al.*, 2005. Anthropogenic mercury emissions in China. *Atmosphere Environment*, 39(40): 7789–7806.

Van Veldhuizen E M, 2000. Electrical Discharges for Environmental Purpose: Fundamentals and Applications. New York: Nova Science Publishers. 50–68.

Yamamoto T, Okubo M, Nagaoka T, Hayakawa K, 2002. Simultaneous removal of NOx, SOx, and CO_2 at elevated temperature using a plasma-chemical hybrid process. *IEEE Transactions on Industry Applications*, 38(5): 1168–1173.

Yan K P, Hui H X, Cui M, Miao J S, Wu X L, Bao C G, 1998. Corona induced non-thermal plasmas: Fundamental study and industrial applications. *Journal of Electrostatics*, 44(1-2): 17–39.

Yan K P, 2001. Corona plasma generation. Ph.D Thesis. Technische Universtiteit Eindhoven, The Netherlands.

Zeng H C, Jin F, Guo J, 2004. Removal of elemental mercury from coal combustion flue gas by chloride-impregnated activated carbon. *Fuel*, 83(1): 143–146.