

## Gaseous Elemental Mercury Oxidation by Non-thermal Plasma

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**Abstract:** The effects of the discharge tooth wheel number and the concentrations of CO<sub>2</sub>, NO and SO<sub>2</sub> in the simulated flue gas on elemental mercury oxidation by non-thermal plasma were investigated by using a link tooth wheel-cylinder reactor energized by a negative high voltage DC power supply. The results indicated that a significant amount of elemental mercury was oxidized by non-thermal plasma. And the total mercury concentration of reactor outlet decreased as the discharge voltage increased. When the number of the discharge tooth wheel increased, more elemental mercury could be oxidized and more energy was injected into the plasma reactor. The spark voltage enhanced with the increase of CO<sub>2</sub> concentration and the discharge voltage corresponding to the same elemental mercury oxidation rate also increased. The presence of SO<sub>2</sub> resulted in a significant decrease of outlet total mercury concentration. NO restrained the oxidation of elemental mercury and the removal of mercury.

**Keywords:** Non-thermal plasma, flue gas, elemental mercury oxidation, mercury removal

### 1 INTRODUCTION

Mercury is one of the most important trace elements at a global scale due to its toxic effects on both the environment and human health. Since 1990s, the concentration of mercury in the environment has been increasing. Global emissions of anthropogenic mercury to the atmosphere have been estimated to be 2190 tons in 2000, of which 65% was from coal combustion. In China, coal combustion is the main source of electricity and heat production, so the amount of mercury emitted from coal-fired electric utilities can not be neglected. Statistics shows that mercury emissions from all sorts of sources to the air in China were 650 tons in 2003, and the coal-fired related mercury emissions accounted for 39% of the total emissions [9].

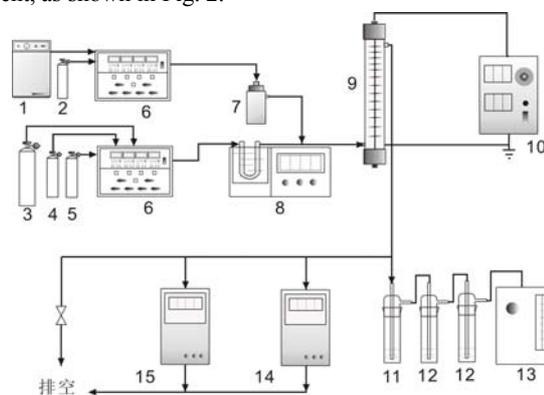
Considerable studies have been conducted regarding mercury control in emissions from coal-fired electric utilities. Studies have shown that the removal of mercury mainly depends on the species of mercury in the flue gas. Most of the particulate-bound mercury can be captured by an electrostatic precipitator or a fabric filter. Gaseous oxidized mercury (Hg<sup>2+</sup>) can be removed by the wet flue gas desulphurization (WFGD) and the removal efficiency can reach 85%-90% because of its high water-solubility. But the removal of elemental mercury vapor (Hg<sup>0</sup>) by conventional WFGD is not promising, because it is highly volatile and water-insoluble. Hg<sup>0</sup> has to be adsorbed by sorbents or converted to oxidized form ahead of the WFGD. Nowadays, the combination of precipitator and adsorption by activated carbons is considered to be an effective method in mercury removal [6]. However, the high carbon-to-mercury weight ratios and difficulties in sorbents regeneration result in the unacceptable high cost, thus limit the extensive application of this method. Photochemical oxidation is a novel method to remove mercury. It introduces ultraviolet (UV) light into flue gas, and results in the conversion of Hg<sup>0</sup> to Hg<sup>2+</sup> [4]. However, the oxidation rate of photochemical is very limited.

Recently, non-thermal plasma technology has been used for the oxidation of the NO<sub>x</sub>, SO<sub>2</sub>, and volatile organic compounds (VOCs), leading to some very promising results [2,5]. In the fields of mercury removal by non-thermal plasma, some tentative researches have been conducted [3]. However, systematic study concerning mercury transformation and removal in the presence of multiple pollutants is not available now. In this paper, a non-thermal plasma system using a link tooth wheel-cylinder reactor was used to investigate the effects of the discharge condition and the concentrations of CO<sub>2</sub>, SO<sub>2</sub> and NO on the elemental mercury oxidation.

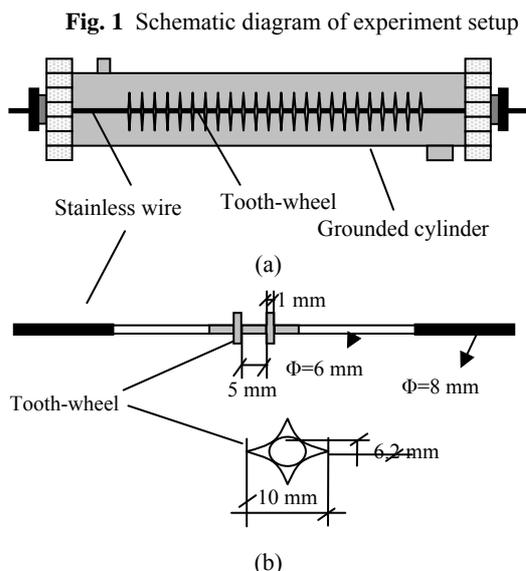
### 2 EXPERIMENTAL

#### 2.1 Experiment Setup

The bench-scaled experimental setup schematic diagram is shown in Fig. 1. The plasma reactor energized by a negative DC power supply is in a wire-to-cylinder electrode arrangement, as shown in Fig. 2.



1. Air compressor, 2. CO<sub>2</sub> cylinder, 3. N<sub>2</sub> cylinder, 4. SO<sub>2</sub> cylinder, 5. NO cylinder, 6. Mass flow controller, 7. Bubble tower, 8. Mercury permeation tube, 9. Plasma reactor, 10. High voltage power supply, 11. Hg<sup>2+</sup> sampling tube, 12. Hg<sup>0</sup> sampling tube, 13. Air sampler, 14. NO<sub>x</sub> analyzer, 15. SO<sub>2</sub> analyzer



**Fig. 2** Schematic diagram of the plasma reactor

As shown in Fig. 2(a), the discharge electrode is a stainless steel pipe linked tooth wheels equidistantly. 28 tooth wheels were used in the research unless stated specially. The grounded electrode is a cylinder with an inner diameter of 42 mm. 4 discharge points are evenly distributed on each tooth wheel, as shown in Fig. 2(b).

## 2.2 Experiment Method

The elemental mercury was introduced to the gas mixture via a temperature-controlled mercury permeation tube. Water was delivered to the gas mixture via a temperature-controlled bubble tower. All gas components were mixed completely before the reactor. The basic constituents of the simulated flue gas were 6% O<sub>2</sub>, 12% CO<sub>2</sub>, 2.3% H<sub>2</sub>O and 115±5 ng/L Hg, using N<sub>2</sub> as balance gas, unless stated especially, the total flow rate was 3 L/min. Heating tapes were used along the pipelines after the mercury permeation tube to maintain the gas temperature at 80±1°C, so to simulate the actual condition of flue gas and prevent the condensation of mercury vapor. Sampling points were placed at both inlet and outlet of the plasma reactor. Non-thermal plasma formed when high voltage was supplied between the active electrode and cylinder grounded electrode.

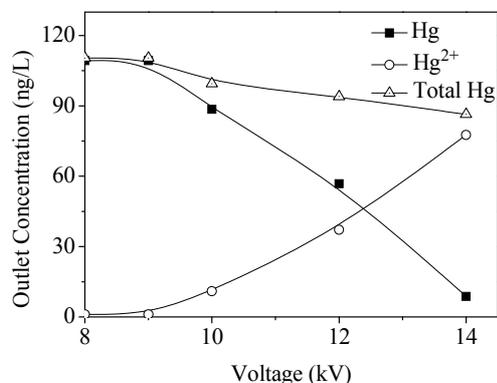
In this research, mercury was analyzed by the Dithizone Spectrophotometric method. Oxidized mercury was absorbed by 0.5 mol/L sulfuric acid. Elementary mercury was absorbed by a mixture of 0.1 mol/L potassium permanganate and 10%v/v sulfuric acid. SO<sub>2</sub> and NO were measured by a SO<sub>2</sub> analyzer (Kane Corp. Model SGA94-SO<sub>2</sub>) and a flue gas analyzer (Testo Corp. Model 335-NO-NO<sub>2</sub>) respectively.

## 3 RESULTS AND DISCUSSION

### 3.1 Effect of Applied Voltage on Elemental Mercury Oxidation

The effect of applied voltage on elemental mercury oxidation was firstly investigated in the basic simulated flue

gas. As shown in Fig. 3, elemental mercury oxidation occurs when the voltage is above 9 kV. And oxidation rate enhances with the increase of applied voltage. When the voltage is 14 kV, approximate 92 percent of elemental mercury is oxidized. When the applied voltage exceeds 15 kV, the discharge becomes unstable.



**Fig. 3** Effect of applied voltage on elemental mercury oxidation

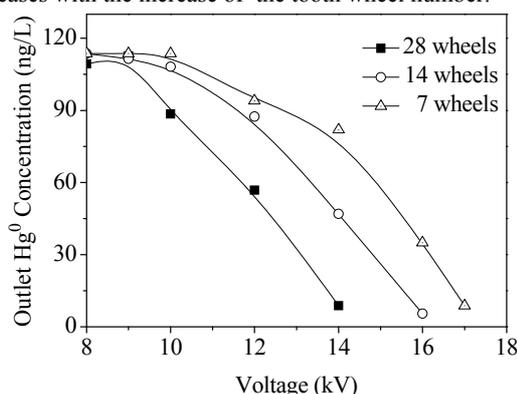
It is clear that the increase of energy input promotes the formation of free radicals such as O, N, and O<sub>3</sub>. Elemental mercury is oxidized by these radicals via following reactions [4,10].

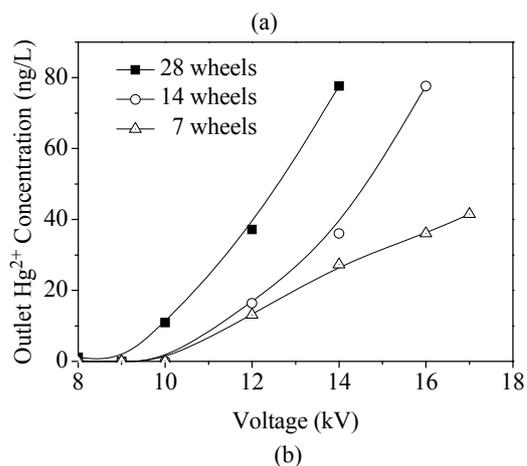


Fig. 3 also shows that the total mercury concentration of reactor outlet decreases as the applied voltage increases. This may be due to the deposition of mercury on the inner wall of plasma reactor under high electric field strength. Similar phenomenon was reported in previous studies [3].

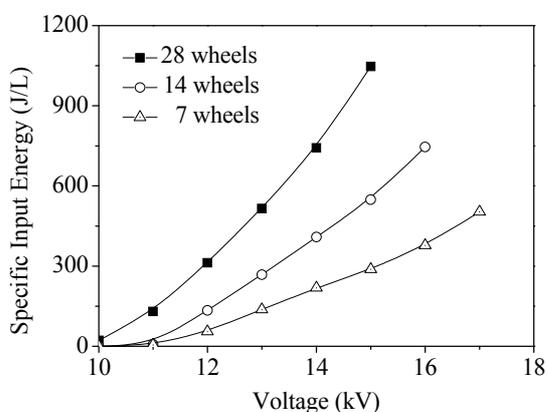
### 3.2 Effect of Tooth Wheel Number on Elemental Mercury Oxidation

Fig. 4(a) and Fig. 4(b) respectively give the relationship between the outlet concentration of Hg<sup>0</sup> or Hg<sup>2+</sup> and applied voltage under the basic constituents of the simulated flue gas. It can be seen that the tooth wheel number has a significant effect on elemental mercury oxidation. The oxidation of elemental mercury enhances as the tooth wheel number increases. A possible reason is that when the tooth wheel number increases, more energy is injected into the plasma reactor. As shown in Fig. 5, specific input energy (SIE) increases with the increase of the tooth wheel number.





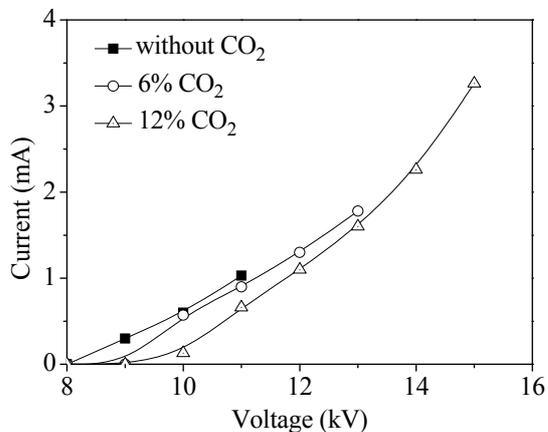
**Fig. 4** Relationship between concentrations of outlet  $\text{Hg}^0$  (a) or  $\text{Hg}^{2+}$  (b) and applied voltage under different tooth wheel numbers



**Fig. 5** Relationship between specific input energy and applied voltage under different tooth wheel numbers

### 3.3 Effect of Inlet $\text{CO}_2$ Concentration on Elemental Mercury Oxidation

The effect of  $\text{CO}_2$  concentration on voltage-current characteristics was firstly investigated in the presence of 6%  $\text{O}_2$ , 2.3%  $\text{H}_2\text{O}$  and  $\text{CO}_2$  with different concentrations, using  $\text{N}_2$  as balance gas. Fig. 6 shows the voltage-current curves corresponding to the inlet  $\text{CO}_2$  concentrations of 0, 6% and 12% respectively.



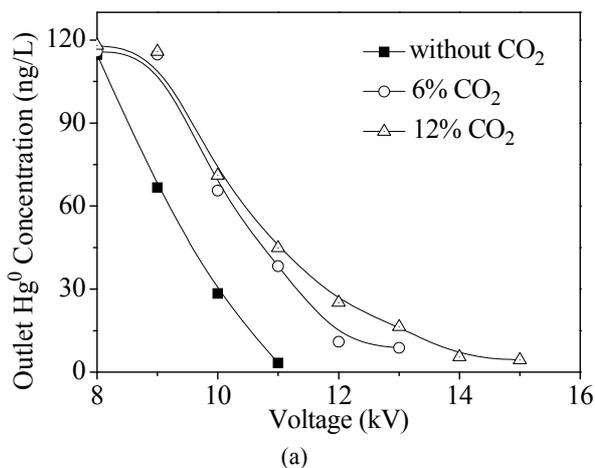
**Fig. 6** Voltage-current curves corresponding to different inlet  $\text{CO}_2$  concentrations

It can be seen from Fig. 6 that 11 kV, 13 kV and 15 kV are the highest voltages which maintains stable discharge, corresponding to the inlet  $\text{CO}_2$  concentrations of 0, 6% and 12%. It is clear that  $\text{CO}_2$  plays an important role in stabilizing discharge process. The more inlet  $\text{CO}_2$  concentration is, the higher the spark voltage is.

The outlet concentrations of  $\text{Hg}^0$  and  $\text{Hg}^{2+}$  as a function of the applied voltage are shown in Fig. 7(a) and Fig. 7(b) when the inlet  $\text{CO}_2$  concentrations are 0, 6% or 12%, respectively. It can be seen that the inlet  $\text{CO}_2$  concentration has almost no effect on the maximum oxidation rate. The outlet  $\text{Hg}^0$  and  $\text{Hg}^{2+}$  concentrations, corresponding to the highest voltages of three different inlet  $\text{CO}_2$  concentrations, are almost the same. However, the applied voltage enhances with the increase of inlet  $\text{CO}_2$  concentration for the same oxidation rate (the same outlet  $\text{Hg}^0$  and  $\text{Hg}^{2+}$  concentrations). On the basis of theoretical analysis, CO is formed because  $\text{CO}_2$  reacts with electron and N during discharge process [1].



Actually, in this research, it was noticed that the outlet CO concentration increased with the increase of inlet  $\text{CO}_2$  concentration.

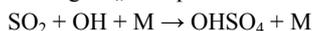


**Fig. 7** Relationship between outlet  $\text{Hg}^0$  (a) or  $\text{Hg}^{2+}$  (b)

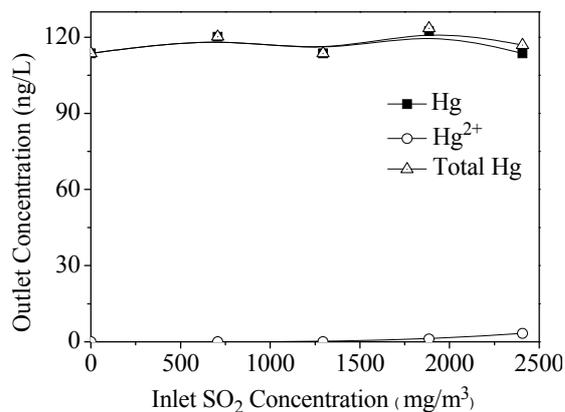
concentrations and applied voltage under different inlet  $\text{CO}_2$  concentrations

### 3.4 Effect of Inlet $\text{SO}_2$ Concentration on Elemental Mercury Oxidation

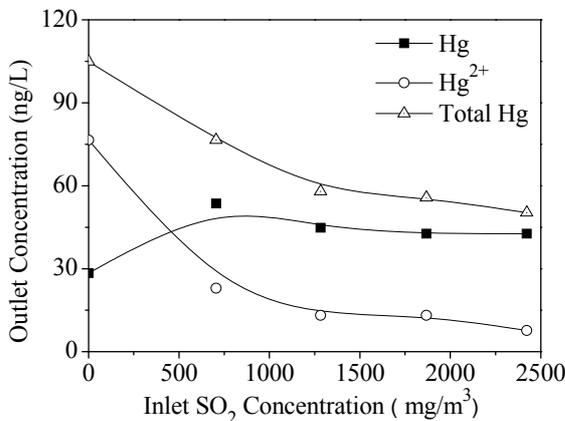
The effect of inlet  $\text{SO}_2$  concentration on elemental mercury oxidation was studied under different applied voltages. Fig. 8 (a) and Fig. 8 (b) give the relationship between the outlet mercury concentration and inlet  $\text{SO}_2$  concentration corresponding to the applied voltage of 0 kV and 14 kV. It can be seen from Fig. 8 (a) that the elemental mercury oxidation doesn't happen and total mercury concentration doesn't change as the increase of inlet  $\text{SO}_2$  concentration when high voltage is not applied to the plasma reactor. But the presence of  $\text{SO}_2$  results in a slight increase of  $\text{Hg}^0$  concentration when the applied voltage is 14 kV, as shown in Fig. 8 (b). This may be due to the decrease of active radicals used to oxidize the elemental mercury because  $\text{SO}_2$  reacts with radicals and  $\text{SO}_3$  was formed [8]. Fig. 8(b) also shows that both total mercury and  $\text{Hg}^{2+}$  concentrations significantly decrease as the inlet  $\text{SO}_2$  concentration increases, which is attributed to that  $\text{SO}_3$  reacts with the oxidized mercury to form  $\text{HgSO}_4$ , as reported in Schofield's paper [7].



(M is other particle in the system) (5)



(a)



(b)

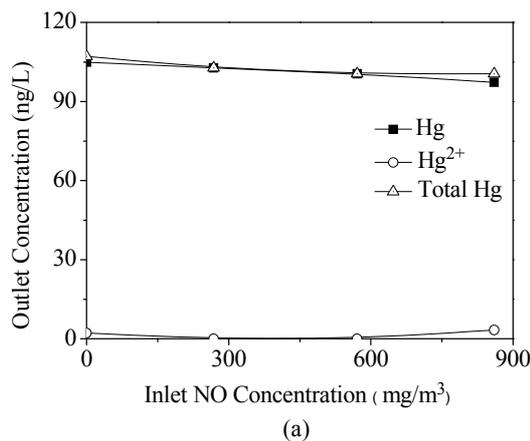
Fig. 8 Relationship between outlet mercury

concentration and inlet  $\text{SO}_2$  concentration under 0 kV (a) and 14 kV (b)

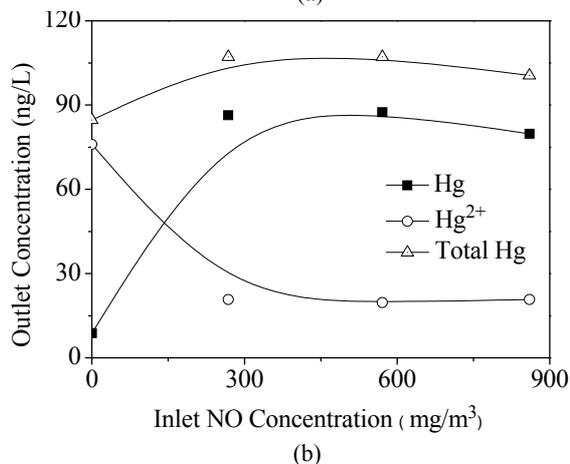
Actually, it was noticed that there existed a significant amount of deposits on the inner wall of the non-thermal plasma reactor and the downstream pipeline after this reactor. And  $\text{Hg}^{2+}$  and  $\text{SO}_4^{2-}$  were detected in the liquor when the inner wall was washed by deionized water.

### 3.5 Effect of Inlet NO Concentration on Elemental Mercury Oxidation

Fig. 9(a) and Fig. 9(b) give relationship between outlet mercury concentration and inlet NO concentration under 0 kV and 14 kV.



(a)



(b)

Fig. 9 Relationship between outlet mercury concentration and inlet NO concentration under 0 kV (a) and 14 kV (b)

It can be seen from Fig. 9(a) that the addition of NO has almost no effect on elemental mercury oxidation under 0 kV. When high voltage of 14 kV is applied to the plasma reactor, the presence of NO restrains elemental mercury oxidation. The elemental mercury concentration increases from 10 ng/L to 86 ng/L and oxidized mercury concentration decreases from 76 ng/L to 20 ng/L as NO concentration increases from 0  $\text{mg}/\text{m}^3$  to 268  $\text{mg}/\text{m}^3$ . Above 268  $\text{mg}/\text{m}^3$ , further increase of NO concentration no longer affects elemental mercury oxidation significantly. This may be due to the fact that elemental mercury is oxidized mainly by radicals formed in the discharge process. However, NO would consume some of

the radicals, as shown in the following reactions, thus results in a reduction of radicals reacted with elemental mercury [8].



In the experiment, it was also found that when the applied voltage was 14 kV, as inlet NO concentration increased, the outlet NO<sub>2</sub> concentration accordingly increased and the outlet O<sub>3</sub> concentration decreased.

#### 4 CONCLUSIONS

(1) Under the simulated flue gas condition, the reactive radicals induced by high voltage negative DC discharge can oxidize elemental mercury. The mercury oxidation rate could be higher than 90%.

(2) As the number of the discharged tooth wheel increases, more energy is injected into the plasma reactor and more elemental mercury is oxidized.

(3) CO<sub>2</sub> in the simulated flue gas plays an important role in stabilizing discharge process. The spark voltage increases with the increase of CO<sub>2</sub> concentration.

(4) SO<sub>2</sub> promotes the mercury removal. Both outlet oxidized mercury concentration and total mercury concentration decrease as SO<sub>2</sub> concentration increases. The presence of NO restrains the oxidation of elemental mercury.

#### ACKNOWLEDGEMENTS

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