Oxidation efficiency of elemental mercury in two DBD plasma reactors

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Abstract. Configuration of plasma reactors influences the generation of active species including the energized electrons, active radicals and the distribution of active species in reactor, and thus influences the removal efficiency of pollutants. Oxidation efficiency of elemental mercury (Hg0) in two different DBD plasma reactors was studied in this paper. One plasma reactor is a surface discharge reactor (SDR) with a spiral stainless steel thread as the high voltage electrode, and the other plasma reactor is a concentric cylinder type DBD reactor (CCDR) with a copper screw rod as the high voltage electrode. The oxidation efficiencies of Hg0 under different specific energy density (SED), oxygen content, flue gas residence time and the temperature of flue gas indicate that SDR had a better performance than CCDR in oxidation of Hg0, which can be attributed to the higher generation efficiency of ozone in SDR than in CCDR.

1. Introduction
The combustion of fossil fuels, especially coal, often emits pollutants such as SO2, NOx, heavy metals including Hg and As, and so on. Since fossil fuels contain many natural elements including sulfur (S), mercury (Hg) and arsenic (As). Hg emission can also bring serious harms to organisms and humans during its transfer and conversion in nature. So control of mercury emission is very important and necessary.

In recent years, active carbon adsorption [1], photocatalysis and adsorption [2], catalytic oxidation [3] etc have been studied to purify the flue gas containing Hg. Adsorption of Hg by active carbon is effective on flue gas purification. However, the expensive absorbents limit the application of adsorption process. Moreover, the particle matters, SO2, etc in flue gas might poison the expensive catalysts to the extent to lose its catalytic activity, which results in the difficulty in application of catalysis process to purify flue gas containing Hg.

Non-thermal plasma technologies (NTP) have been studied to abate the pollutants in flue gas [4-10]. During the process of plasma generation, strong oxidative species such as O, ·OH, O3, etc are produced by electrical discharge, which are responsible for oxidation of SO2/NOx/Hg0. The present
studies indicate that non-thermal plasma technologies hold the potential of simultaneously purifying the flue gas containing gaseous pollutants and heavy metal elements.

Dielectric barrier discharge (DBD) is a kind of effective method for production of O₃, one of the important species for oxidation of Hg⁰. In this paper, the effect of electrode configuration on the purifying efficiency of flue gas containing Hg⁰ was studied. One of the electrode configurations was a typical concentric cylinder DBD type reactor (CCDR), and the other was a surface discharge reactor (SDR). The Hg⁰ oxidation efficiency in the two different DBD plasma reactors was compared, and the reason of different Hg⁰ purification efficiency of two DBD reactors was analyzed.

2. Experimental

2.1. Experimental method
Removal of Hg⁰ from simulated flue gas was conducted in two DBD plasma reactors, and the schematic of Hg⁰ removal process was shown in figure 1. The simulated flue gas was synthesized by air and Hg⁰ vapor. The Hg⁰ vapor was generated by liquid Hg⁰ bubbling method with N₂ as carrier gas, in which a bottle containing liquid Hg⁰ was put into water bath (306 K) to keep a stable evaporation rate of Hg⁰. The Hg⁰ concentration was regulated by controlling the flow rates of air and N₂ carrier gas. Flue gas sampled at the outlet of plasma reactor was analyzed by Ontario Hydro Method (OHM) [11], and then analyzed by Lumex RA-915+ and RP91. All the chemicals used for analysis of samples were analytically pure.

2.2. DBD plasma reactors

One of the plasma reactors, illustrated in figure 2 (a), was a typical concentric cylinder type DBD reactor, in which a copper screw rod with a diameter of 5.5 mm was fixed at the centre of a quartz glasses tube. The inner diameter and the wall thickness of quartz glasses tube was 12 mm and 3 mm, respectively. The copper rod was used as high voltage electrode and the quartz tube wrapped in foil.
was grounded. The effective zone of plasma generation was about 200 mm in length.

The other plasma reactor, illustrated in figure 2 (b), was a surface discharge reactor, in which a spiral electrode made of stainless steel of 1 mm diameter was used as the high-voltage electrode. The high-voltage electrode was attached tightly to the inside wall of the cylindrical quartz tube with an outer diameter 15 mm and an inner diameter 12 mm and a length of 260 mm. A silver paper with a length of 200 mm wrapping outside the quartz tube was used as the ground electrode. In the two plasma reactors, the high voltage electrodes were supplied by an AC power supply of 50 Hz.

2.3. Measurement method
The discharge voltage and discharge current waveforms were measured by a digital oscilloscope (TDS2014, Tektronix) equipped with a high voltage probe (P6015A, Tektronix) and a current probe (A6021, Tektronix). The consumed discharge energy of DBD reactor was obtained by voltage-charge curve (Lissajous figure). The charge was measured using a capacitor (2 μF) inserted between the reactor and the ground.

3. Results and Discussion
Configuration of discharge reactors has an important influence on the generation of active species and their distribution in reactor, and thus impact the removal of pollutants. The removal efficiency of Hg\(^0\) in two different DBD reactors under different conditions including specific input energy, residence time, O\(_2\) content and the temperature of flue gas was studied.

The oxidation removal rate of Hg\(^0\) under different specific energy density (SED) was shown in figure 3, and SED was calculated by equation (1).

\[
\text{SED} (J \text{ L}^{-1}) = \frac{P}{Q} 
\]

(1)

Where \(P\) (W) and \(Q\) (L s\(^{-1}\)) was the input power and the flow rate of simulated flue gas, respectively.

![Figure 3. Hg\(^0\) oxidation efficiency in two DBD reactors.](image)

![Figure 4. O\(_3\) generated in two DBD reactors.](image)

In this experiment the flow rate of flue gas was 4.5 L min\(^{-1}\), and the initial concentration of Hg\(^0\) was 110 μg m\(^{-3}\). The oxidation efficiency (\(\eta\)) of Hg\(^0\) was calculated according to the equation (2).

\[
\eta = (1 - C_t / C_0) \times 100\%
\]

(2)

Where \(C_t\) and \(C_0\) was the concentration of Hg\(^0\) (μg m\(^{-3}\)) at any time and the initial concentration, respectively.
Figure 3 indicates that removal of Hg\(^0\) increased with the SED both in SDR and CCDR. Figure 3 also indicates that higher removal rate of Hg\(^0\) was obtained with the surface discharge reactor under the same SED, and the Hg\(^0\) oxidation efficiency in SDR was about 8%~20% higher than that in CCDR.

When the voltage exerted on discharge electrode is high enough, electrical discharge is initiated between the electrodes and leads to the production of energized electrons. During the collision of energized electrons and background gas (e.g. air), active species including O, ·OH and O\(_3\) will be generated by the dissociation and excitation of air. Since O\(_2\) is the important species for Hg\(^0\) oxidation, the higher generation quantity of O\(_3\) by surface discharge reactor can explain the phenomenon that higher Hg\(^0\) removal was gained by SDR, and the measurement result of ozone concentration testified our speculation. The data shown in figure 4 indicates that the ozone concentration produced by SDR was 3 ~ 9 times higher than by CCDR.

Figure 5 shows the removal rate of Hg\(^0\) under different oxygen content. The flow rate of flue gas and the initial concentration of Hg\(^0\) were similar to that in figure 3. Figure 5 presents a similar phenomenon like in figure 3, namely, higher Hg\(^0\) oxidation removal rate was obtained by SDR even under lower SED. Under a SED of 5.93 J L\(^{-1}\), the Hg\(^0\) removal rate in SDR could be improved by 4%~10% than that in CCDR under a SED of 12.1 J L\(^{-1}\). The experiment in figure 5 also demonstrates the higher removal efficiency of Hg\(^0\) could be obtained by surface discharge reactor.

![Figure 5. Hg\(^0\) oxidation efficiency under different oxygen contents.](image)

![Figure 6. Hg\(^0\) oxidation efficiency under different residence time of flue gas.](image)

![Figure 7. SED corresponding to the experiment in fig.6.](image)

Figure 6 and figure 7 show the removal rate of Hg\(^0\) and SED values under different residence time, respectively. Figure 6 shows that the removal rate of Hg\(^0\) in SDR and CCDR differed very little, but
figure 7 indicates that the SED value in SDR was far lower than that in CCDR. The results in figure 6 and 7 show that almost the same removal rate can be obtained under lower SED in SDR than in CCDR, which indicates the energy efficiency of Hg$^0$ removal in SDR was higher than CCDR.

![Figure 8](image1.png)  
**Figure 8.** Effect of temperature of flue gas on Hg$^0$ oxidation efficiency in SDR.

![Figure 9](image2.png)  
**Figure 9.** Effect of temperature of flue gas on Hg$^0$ oxidation efficiency in CCDR.

Temperature of flue gas has important influence on the discharge characteristics and ozone production. Since the decomposition of ozone speeds up with the increasing temperature, the high temperature should be disadvantageous for oxidation of Hg$^0$ in flue gas. Figure 8 and figure 9 demonstrate the disadvantageous influence of high temperature on Hg$^0$ oxidation. In addition, higher Hg$^0$ oxidation efficiency was obtained by SDR under the same applied voltage when comparing with CCDR.

4. Conclusions

Oxidative removal of Hg$^0$ from simulated flue gas was conducted in two DBD plasma reactors. The experimental results indicate that higher oxidation efficiency of Hg$^0$ could be obtained in a surface discharge reactor than in a concentric cylinder DBD plasma reactor, which mainly contributed to the higher ozone concentration produced by surface discharge reactor. Decomposition of ozone speeds up with the increasing temperature, so the high temperature is disadvantageous for oxidation of Hg$^0$ in flue gas.

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