Performance evaluation of non-thermal plasma injection for elemental mercury oxidation in a simulated flue gas

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HIGHLIGHTS

- The use of non-thermal plasma injection approach to oxidize Hg^0 in simulated flue gas at 110 °C was studied.
- A high Hg^0 oxidation efficiency was observed in the mixed flue gas that included O_2, H_2O, SO_2, NO and HCl.
- Chemical and physical processes (e.g., ozone, N_2 metastable states and UV-light) contributed to Hg^0 oxidation.
- Mercury species mainly existed in the form of HgO(s) adhering to the suspended aerosols in the gas-phase.

GRAPHICAL ABSTRACT
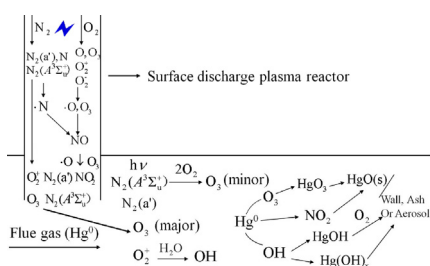
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ABSTRACT

The use of non-thermal plasma (NTP) injection approach to oxidize elemental mercury (Hg^0) in simulated flue gas at 110 °C was studied, where a surface discharge plasma reactor (SDPR) inserted in the simulated flue duct was used to generate and inject active species into the flue gas. Approximately 81% of the Hg^0 was oxidized and 20.5 μg kJ^{-1} of energy yield was obtained at a rate of 3.9 J L^{-1}. A maximal Hg^0 oxidation efficiency was found with a change in the NTP injection air flow rate. A high Hg^0 oxidation efficiency was observed in the mixed flue gas that included O_2, H_2O, SO_2, NO and HCl. Chemical and physical processes (e.g., ozone, N_2 metastable states and UV-light) were found to contribute to Hg^0 oxidation, with ozone playing a dominant role. The deposited mercury species on the internal surface of the flue duct was analyzed using X-ray photoelectron spectroscopy (XPS) and electronic probe microanalysis (EPMA), and the deposit was identified as HgO. The mercury species is thought to primarily exist in the form of HgO(s) by adhering to the suspended aerosols in the gas-phase.

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1. Introduction

Coal combustion is the greatest anthropogenic source of toxic air pollutants [1]. Every year, tons of SO_2, NOx and heavy metals, including mercury and arsenic are released into the air. Mercury is of significant concern because of its toxicity, mobility in the food chain, and the issues related to its bioaccumulation [2]. Coal-fired power plants are the largest source of anthropogenic mercury

emissions, accounting for approximately one-third of the 150 tons of annual mercury emission in the U.S., and mercury was the first heavy metal regulated by the U.S. Environmental Protection Agency (EPA) in the coal-fired power plants [3]. By December 2011, the U.S. EPA announced the Mercury and Toxic Standards to protect American families from the power plant emissions of mercury and toxic air pollution [4]. As one of the largest coal producers and consumers in the world, China accounts for 48.2% of the coal combustion in the world and releases large amounts of Hg. The Chinese government has paid much attention to Hg emission and mandated that the emission of mercury and its compounds should be less than 0.03 mg m^{-3} after 2015.

In the coal-fired flue gas, mercury exists in three forms: elemental mercury (Hg^0), oxidized mercury (Hg^{2+}), and particulate-bound mercury (Hg^p) [5]. Hg^{2+} and Hg^p are relatively easy to remove from flue gas using conventional air pollution control devices (APCDs). Hg^{2+} is removed with high efficiency using wet flue gas desulfurization equipment due to its high water-solubility, and Hg^p is easily captured, along with fly ash particles, in electrostatic precipitators (ESPs) and/or baghouses. Hg^0 is unlikely to be removed using downstream APCDs because it tends to be water insoluble [5]. Recently, several techniques have been used in attempts to reduce Hg^0 emission, such as powder activated carbon (PAC) injection [6,7], catalytic oxidation [8,9] and oxidant injection [10], which usually suffers from the problems of high cost and high carbon-to-mercury ratio of the PAC injection, the deactivation of the catalysts and the instability of the injected oxidants. Therefore, it is imperative to develop cost-effective and highly efficient approaches to oxidize Hg^0 in coal-fired flue gas.

The use of non-thermal plasma (NTP) in the removal of NOx, SO$_2$ and Hg^0 has aroused considerable interest [11–14]. Compared with other mercury control technologies, the NTP approach is a much more attractive and economical approach to oxidize Hg^0 [15–18]. Investigations on Hg^0 oxidation in flue gas using a pulse-corona discharge were performed by Masuda et al. [15] and Helfrich et al. [18]. Dielectric barrier discharges (DBDs) have received the most extensive investigation on Hg^0 oxidation due to the method's stable discharge features and highly effective production of plasma. Chen et al. [19] investigated the effect of gas components on Hg^0 oxidation using DBD. Byun et al. [20] discussed the Hg^0 oxidation mechanism using DBD. One of the common features of the above-mentioned DBD methods, referred to as "direct oxidation", is that the flue gas is directly passing through the reactor. However, direct Hg^0 oxidation methods have some drawbacks. For example, the metal electrodes may be eroded by acidic gases, and the residual fly ash not collected by ESPs can adhere to the surface of electrodes and become charged in the reactor, thereby adversely influencing on the electric discharge. In particular, the obvious drawback of "direct oxidation" is that a plasma reactor of large volumes is required when purifying a high flow rate flue gas, which results in the increasing construction cost for the flue gas treatment equipment. Considering these limitations and drawbacks of direct oxidation methods, NTP injection was proposed to oxidize Hg^0.

For NTP injection, the plasma reactor is inserted into the simulated flue duct and the active species are generated in the plasma reactor under the condition of a low NTP injection gas flow rate; the active species are subsequently injected into the flue gas. Compared with "direct oxidation", the investment cost and system size are reduced significantly because large plasma reactors are not required. However, to date, little has been reported regarding the oxidation of Hg^0 in a coal-fired flue gas using NTP injection. This work studied a novel approach using non-secondary pollution for the efficient oxidation of Hg^0 in coal-fired flue gas.

2. Experimental

2.1. Experimental setup

The schematic of the experimental setup is shown in Fig. 1. Fig. 1(A) shows that the setup consisted primarily of a reactor system with a power supply, gas mixture supply and analytical instruments. AC voltage (50 Hz) with a peak value varying from 12 to 20 kV was applied in the discharge reactor to produce the plasma. Schematic diagrams of NTP injection and direct oxidation are presented in Fig. 1(B) and (C), respectively. A surface discharge plasma reactor (SDPR) was a concentric cylinder, which had a quartz tube (outer diameter 15 mm, inner diameter 12 mm, and length 260 mm) with two electrodes. The high-voltage electrode was a spiral electrode made of stainless steel with a 1 mm diameter and attached tightly to the inside wall of the quartz tube. The ground electrode (length 200 mm) was made of a stainless mesh wrapping outside the quartz tube. The SDPR was inserted into the simulated flue duct composed of a quartz tube (outer diameter of 45 mm, inner diameter of 42 mm, and length of 1000 mm), and the discharge length of the SDPR in the simulated flue duct was approximately 15 mm. For NTP injection, the active species generated in the SDPR were injected into the simulated flue duct to oxidize Hg^0, while for direct oxidation, the flue gas was directly introduced into the SDPR. To study the contribution of O$_3$ in Hg^0 oxidation, a Hg^0 oxidation experiment using ozonation was performed. A schematic diagram of the experimental setup for ozonation is shown in Fig. 1(D). The O$_3$ concentration was equal to that obtained by NTP injection under air atmosphere, and the O$_3$ concentrations increased from 5.12 to 8.68 μg L^{-1} with an increase in the applied voltage from 12 to 20 kV at 1.2 L min^{-1}. In the NTP injection system, to study the contribution of UV-light in Hg^0 oxidation, the outlet of the SDPR was plugged to cause a 0 L min^{-1} flow rate of the NTP injection gas. Next, NOx was produced in the discharge process under air atmosphere to investigate the background NOx concentration; the reference experiments were conducted, and only NO$_2$ was detected, with the NO$_2$ concentrations increasing from 8 to 24 ppm with an increase in the applied voltage from 12 to 20 kV. In the reference experiments, clean air was input into the SDPR and the simulated flue duct at 110 °C.

2.2. Experimental methods

The peak voltage and current were measured using an oscilloscope (Tektronix TDS2014) equipped with a voltage probe (Tektronix P6015A) and a current probe (Tektronix P6021). The voltage–charge (V–Q) Lissajous method was used to determine the discharge power (W). All of the experiments were performed at a simulated flue gas flow rate of 27 L min^{-1} and a flue gas temperature of 110 °C. When the flow rate of the NTP injection gas varied from 0.8 to 3.0 L min^{-1}, the corresponding time for the active species injecting into the flue duct was approximately 45 to 168 ms. Water vapor generated by an evaporator was introduced into the flue gas using air as the carrier, and the humidity of the flue gas was measured using a humidity tester (Rotronic HP22-A + HC2-HK40). A Testo 350 flue gas analyzer (Germany) was used to monitor the concentrations of NOx (NO and NO$_2$), and the detection limit of NOx was 0.1 ppm. A temperature-controlled Dynacal mercury permeation device (VICI Metronic Inc., USA) was used to determine the level of trace mercury vapor and to obtain the desired Hg^0 concentration (100 μg m^{-3}). A RA-915+ mercury analyzer (Lumex, RU) coupled with 10% potassium chloride (KCl) solution was used to measure Hg^0 concentrations. The balance of mercury was measured using a mercury analyzer coupled with RP91 and was conducted in accordance with the ASTM method of Ontario Hydro sampling (ASTM D6784-02) [21]. Ozone was measured using the iodometry method [22], and the Cl$_2$ from the decomposition of HCl