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Pulsed corona discharge for oxidation of gaseous elemental mercury

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Positive pulsed corona discharge has been applied for the oxidation of gaseous elemental mercury (Hg^0) from a simulated flue gas. The oxidation of Hg^0 to HgO and $HgCl_2$ can significantly enhance the mercury removal from flue gas. At a gas condition of O_2 (10%), H_2O (3%), and N_2 (balance), Hg^0 oxidation efficiency of 84% was achieved at an input energy density of 45 J/l. The presence of NO, however, hinders Hg^0 oxidation due to the preferential reaction of NO with O and O_3. On the contrary, SO_2 shows little effect on Hg^0 oxidation due to its preferential reaction with OH. It has been also observed that the HCl in gas stream can be dissociated to Cl and Cl_2 and can induce additional Hg^0 oxidation to $HgCl_2$. © *2008 American Institute of Physics*.
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There is increasing concern over mercury emission due to its environmental and neurological health impact. The largest emission of mercury to the atmosphere occurs from combustion of fossil fuels, mainly coal combustion, which accounts for two-thirds of annual total worldwide anthropogenic emission of approximately 2190 tons.[1] Although the mercury is present in coal in only trace amounts, mercury released into environment can be converted to highly toxic methyl mercury species by natural occurring biological processes. Generally, mercury in flue gas exists in three forms: elemental (Hg^0), oxidized (Hg^{2+}), and particle bound (Hg_p). During coal combustion, mercury is liberated as Hg^0. While Hg^0 passes through combustion and postcombustion zones, some Hg^0 is oxidized, presumably $HgCl_2$ because of an excess of chlorine present in coal.[2] Also, some portion of Hg^0 and Hg^{2+} can be bound to fly ash as particles (Hg_p). Most Hg^{2+} and Hg_p species can be effectively removed by conventional air pollution control systems (wet scrubbers, fabric filters, etc.). However, Hg^0 is more difficult to remove due to its high vapor pressure and low water solubility. Hence, it is preferable to oxidize Hg^0 to Hg^{2+} species, such as HgO and $HgCl_2$, for effective mercury emission control.[3]

A promising technology for Hg^0 oxidation is a nonthermal plasma (NTP) process using pulsed corona discharge (PCD). PCD has been studied for several decades and is recognized as a potential process for the simultaneous removal of NO_x and SO_2. Chemically active species such as O, OH, HO_2, and O_3 formed from the electrical discharge can induce the oxidation of NO_x and SO_2 to nitric and sulfuric acids. These acids can then be neutralized by the addition of ammonia.[4] Considering that the mercury content in the flue gas is trivial (below 20 $\mu g/m^3$) compared to the NO_x and SO_2 content, chemically active species from PCD can be expected to show good performance on Hg^0 oxidation along with the removal of NO_x and SO_2. This means that PCD could be a desirable method for mercury treatment as a cobenefit without further energy consumption. For several years, we have attempted commercialization of a NTP process for the removal of NO_x and SO_2 with control of 50 000 N m^3/h of flue gas as a basic module, which is typical of emissions from the sinter plant and industrial waste incinerator in iron and steel making works.[5] The present study has been initiated to gain insight into the physical chemistry of mercury mediated by the plasma environment. The effect of NO and SO_2 on Hg^0 oxidation has been investigated, and additional Hg^0 oxidation by decomposition of HCl in PCD has been studied.

A schematic diagram of the experimental setup for the oxidation of Hg^0 is shown in Fig. 1. A wire-plate type of plasma reactor with 13 tungsten wires of 0.1 mm diameter and two stainless steel plates (90×270 mm^2), which were used as high voltage and ground electrodes, respectively, was kept in an oven to maintain the gas temperature at 90 °C. The distance between the plates is 32 mm, and the tungsten wires are evenly placed between the two plates at intervals of 15 mm. A positive pulse voltage was applied to the reactor by transferring the stored electric energy at a 1.7 nF capaci-

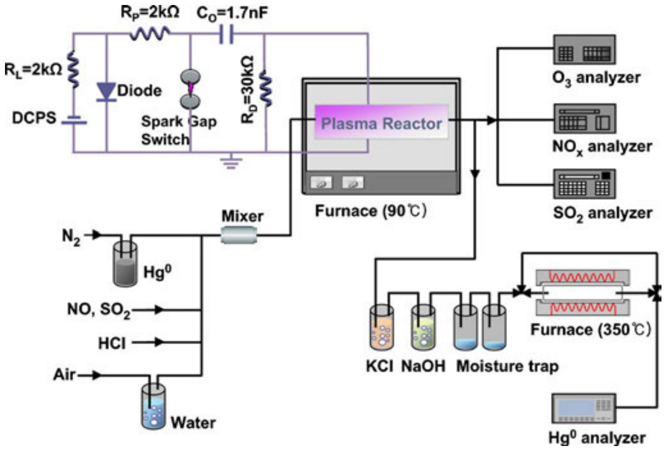

FIG. 1. (Color online) Schematic diagram of the experimental system for Hg^0 oxidation.

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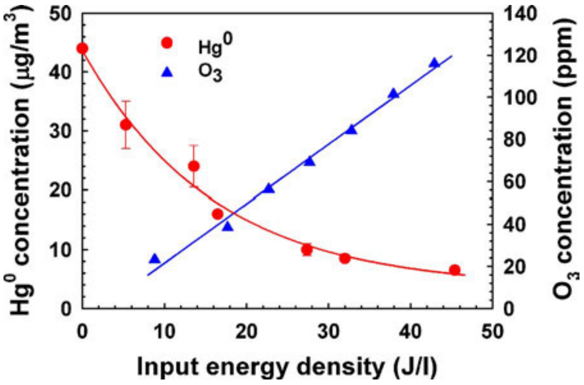

FIG. 2. (Color online) Hg^0 oxidation and O_3 generation as a function of input energy density in the PCD process.

tor by closing the spark gap switch. The applied peak voltage was 17 kV and the maximum current was 32 A with a 0.5 μs width. To investigate the effect of input energy density (the ratio of the power to gas flow rate) on Hg^0 oxidation, the pulse repetition frequency was varied from 5 to 40 Hz. The total gas flow rate was maintained at 3.5 l/min, and the gas stream after plasma reactor passed through KCl and NaOH solutions in turn. The KCl solution captures any oxidized Hg species, while the NaOH solution removes any traces of acid. As a result, only Hg^0 present in the gas stream can enter the Hg^0 analyzer, which adopts the principle of cold vapor atomic absorption spectrometry. A tube furnace (at 350 °C) was placed just before the Hg^0 analyzer for the thermal decomposition of O_3, which would seriously interfere with the Hg^0 measurement by absorbing 253.7 nm of UV light.[6] A moisture trap with a chiller (at 0 °C) was installed to prevent H_2O from condensing in the gas cell of the Hg^0 analyzer.

Pervious reports have concluded that OH, Cl, NO_3, and especially O_3 are the primary sources for Hg^0 oxidation in the atmosphere.[7–9] Although the chemistry of Hg^0 oxidation in the PCD process is different from that of Hg^0 oxidation in atmospheric conditions, O_3 and O species in the PCD process are expected to oxidize Hg^0 into HgO through the following reactions:

$$Hg^0 + O + M \rightarrow HgO + M, \qquad (1)$$

$$Hg^0 + O_3 \rightarrow HgO + O_2. \qquad (2)$$

There is controversy about the effect of OH on Hg^0 oxidation. Some reports claim an important role on Hg^0 oxidation to HgO through HgOH,[10,11] while other reports devalue its role due to the weak Hg–OH bond (~39 kJ/mole) and short HgOH lifetime (~280 μs).[12,13] Our previous study showed that the reaction of Hg^0 with OH to form HgOH does not play a significant role in Hg^0 oxidation in NTP conditions.[14] This may be due to the extremely shorter reaction time and faster decomposition of HgOH in the NTP compared to that in the atmosphere. Figure 2 shows the reduction in Hg^0 concentration and the increase in O_3 concentration in the PCD process as a function of the input energy density, where the O_2 and H_2O content were set to 10% and 3% in N_2. At an input energy density of 45 J/l, the Hg^0 concentration dropped from 45 to 7 $\mu g/m^3$, an oxidation efficiency of 84%. This shows that Hg^0 oxidation is possible in a NTP process. However, because the O_3 concentration at this input energy density is 120 ppm, which is more than 1.7×10^4 times the initial Hg^0 concentration, 45 $\mu g/m^3$ (~7 ppb), it can be inferred that the reaction rate of Hg^0 with O_3 is much slower than that of NO with O_3. Also the energy cost for the oxidation of Hg^0 is about 2.5 MeV/Hg^0 atom, a value which is much higher than that for the oxidation of NO, which is several tens of eV/NO molecule.[15,16] From such a high energy cost for Hg^0 oxidation, it can be deduced that Hg^0 oxidation is hindered in the presence of NO due to its fast reaction with oxidant species O and O_3.

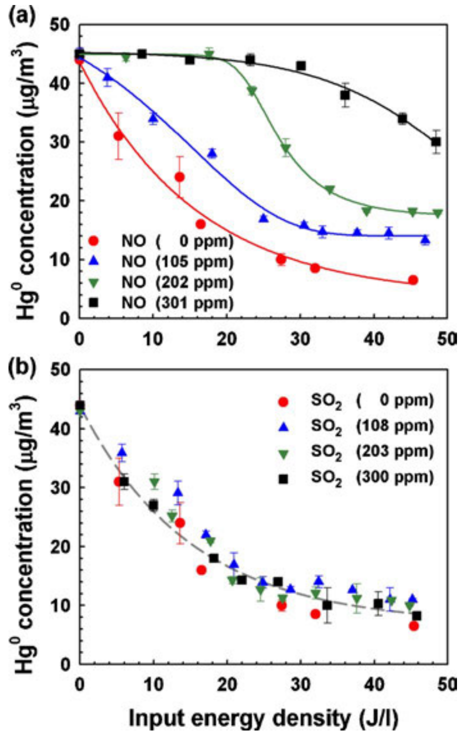

FIG. 3. (Color online) Effect of NO and SO_2 addition on Hg^0 oxidation: (a) reduction of Hg^0 oxidation with respect to NO addition and (b) SO_2 effect on Hg^0 oxidation. Gas conditions: 10% O_2 and 3% H_2O in N_2 balance with 100–300 ppm of NO and SO_2, respectively.

Figure 3(a) shows the effect of NO on Hg^0 oxidation. As expected, the propensity of Hg^0 concentration to oxidation appears to be suppressed markedly as an increasing amount of NO is added to gas flow, and this reduction of Hg^0 oxidation is due to the competitive reaction of NO with O and O_3. Additionally, the effect of SO_2 on Hg^0 oxidation is demonstrated in Fig. 3(b) where an increasing amount of SO_2 is added to the gas flow without addition of NO. It may be seen that unlike NO, SO_2 shows little impact on Hg^0 oxidation. It is well known that most SO_2 is oxidized to HSO_3 and SO_3 by OH and O, not O_3.[17] In fact, the reaction rate of SO_2 with OH is about 100 times faster than that of SO_2 with O radical; thus almost SO_2 is first oxidized by OH to HSO_3, and then finally to H_2SO_4.[17,18] Thus, the consumption of O and O_3 by reaction with SO_2 is very minor due to its fast reaction with OH and, as a result, SO_2 has little effect on Hg^0 oxidation.

Not only O_3 and O but also Cl and Cl_2 can be strong oxidants for Hg^0 in the PCD process. In the plasma process, it is expected that HCl in the gas stream will be dissociated by direct collision with energetic electrons and excited nitrogen molecules, resulting in Hg^0 oxidation to $HgCl_2$ by the following reactions (3)–(8).

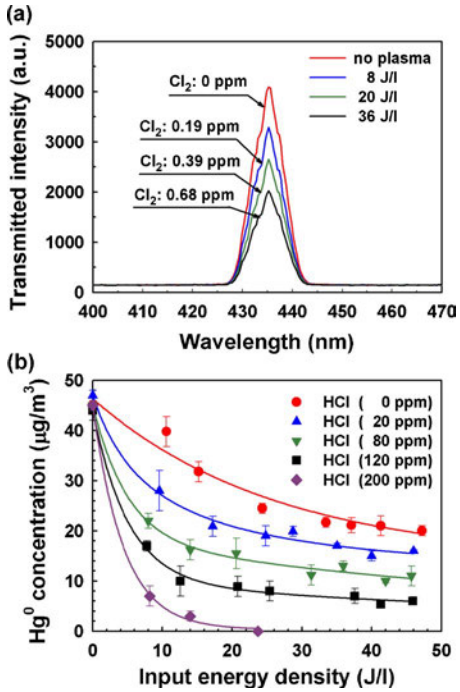

FIG. 4. (Color online) Effect of HCl addition on Hg^0 oxidation: (a) transmitted intensity of light near a wavelength of 435 nm for *ortho*-tolidine solutions obtained by varying the input energy density and (b) promotion of Hg^0 oxidation by HCl addition with gas conditions: 10% O_2 and 3% H_2O in N_2 balance with NO 100 ppm and SO_2 200 ppm.

$$Hg^0 + Cl + M \rightarrow HgCl + M, \tag{3}$$

$$HgCl + Cl + M \rightarrow HgCl_2 + M, \tag{4}$$

$$Cl + Cl + M \rightarrow Cl_2 + M, \tag{5}$$

$$Hg^0 + Cl_2 \rightarrow HgCl + Cl, \tag{6}$$

$$HgCl + Cl_2 \rightarrow HgCl_2 + Cl, \tag{7}$$

$$Hg^0 + Cl_2 + M \rightarrow HgCl_2 + M. \tag{8}$$

In order to verify the decomposition of HCl in the PCD process, an impinger containing 20 ml of *ortho*-tolidine solution was placed at the exit of the plasma reactor. *Ortho*-tolidine is an aromatic organic compound that rapidly reacts with Cl_2 in solution, turning its color from transparent into yellow. The concentration of Cl_2 is qualitatively proportional to the intensity of the color and qualitatively proportional to the absorption of light near a wavelength of 435 nm.[19] In this study, 50 ppm of HCl in N_2 (3.5 l/min) was introduced into the plasma reactor and then passed through the *ortho*-tolidine solution for a 3 min bubbling time at three different energy densities. At all energy densities, it was found that *ortho*-tolidine solution turned yellow, indicating the formation of Cl_2, which is a definite evidence for dissociation of HCl in the PCD process. Figure 4(a) shows the transmitted intensity of light near a wavelength of 435 nm passing each *ortho*-tolidine solution and the corresponding Cl_2 concentrations in the gas stream, where the relation between transmittances and Cl_2 concentrations was calibrated with a Cl_2 permeation tube (VICI Metronics). Although the concentration of Cl_2 produced by the PCD process is minor due to fast recombination of Cl with H to HCl, its concentration is still comparable to that of Hg^0. Thus, Hg^0 oxidation by Cl_2 can be expected in the PCD process, and some portion of Cl atoms can also contribute the Hg^0 oxidation through reactions (3) and (4) rather than recombination into HCl. It is clear from Fig. 4(b) that HCl in the PCD process can cause Hg^0 oxidation, where the Hg^0 oxidation efficiency as a function of input energy density is obtained at four different HCl concentrations with NO 100 ppm and SO_2 200 ppm. Higher concentration of HCl and input energy density result in more generation of Cl and Cl_2, and this gives rise to the better promotion of Hg^0 oxidation to $HgCl_2$. Since the concentraion of HCl in coal-fired flue gas is in the range of 10–100 ppm, it can be concluded that the PCD process effectively leads to the additional oxidation of Hg^0 even at low temperature.

In conclusion, Hg^0 oxidation in the PCD process and the influence of two major pollutants, NO and SO_2, on this process have been investigated. Hg^0 oxidation by O and O_3 can be viable, but it is seriously inhibited in the presence of NO due to the fast reaction of NO with O and O_3. On the other hand, SO_2 shows the little inhibitory effect on Hg^0 oxidation due to the preferential reaction of SO_2 with OH rather than O and O_3. It was also observed that HCl in the PCD process can be dissociated into Cl and Cl_2 by energetic electrons and excited nitrogen species, and this induces the additional Hg^0 oxidation to $HgCl_2$.

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