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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 (Hg0) from a simulated flue gas. The oxidation of Hg0 to HgO and HgCl2 can significantly enhance the mercury removal from flue gas. At a gas condition of O2 (10%), H2O (3%), and N2 (balance), Hg0 oxidation efficiency of 84% was achieved at an input energy density of 45 J/l. The presence of NO, however, hinders Hg0 oxidation due to the preferential reaction of NO with O and O3. On the contrary, SO2 shows little effect on Hg0 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 Cl2 and can induce additional Hg0 oxidation to HgCl2. © 2008 American Institute of Physics.

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 (Hg0), oxidized (Hg2+), and particle bound (Hgpm). During coal combustion, mercury is liberated as Hg0. While Hg0 passes through combustion and postcombustion zones, some Hg0 is oxidized, presumably HgCl2, because of an excess of chlorine present in coal.2 Also, some portion of Hg0 and Hg2+ can be bound to fly ash as particles (Hgpm). Most Hg2+ and Hgpm species can be effectively removed by conventional air pollution control systems (wet scrubbers, fabric filters, etc.). However, Hg0 is more difficult to remove due to its high vapor pressure and low water solubility. Hence, it is preferable to oxidize Hg0 to Hg2+ species, such as HgO and HgCl2, for effective mercury emission control.3

A promising technology for Hg0 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 NOx and SO2. Chemically active species such as O, OH, HO2, and O3 formed from the electrical discharge can induce the oxidation of NOx and SO2 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 μg/m3) compared to the NOx and SO2 content, chemically active species from PCD can be expected to show good performance on Hg0 oxidation along with the removal of NOx and SO2. This means that PCD could be a desirable method for mercury treatment as a cofluid without further energy consumption. For several years, we have attempted commercialization of a NTP process for the removal of NOx and SO2 with control of 50 000 N m3/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 SO2 on Hg0 oxidation has been investigated, and additional Hg0 oxidation by decomposition of HCl in PCD has been studied.

A schematic diagram of the experimental setup for the oxidation of Hg0 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 mm2), 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-

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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. A moisture trap with a chiller (at 0 °C) was installed to prevent H\(_2\)O 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:

\[
\text{Hg}^0 + O + M \rightarrow \text{HgO} + M, \tag{1}
\]

\[
\text{Hg}^0 + O_3 \rightarrow \text{HgO} + O_2. \tag{2}
\]

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\(_3\) and H\(_2\)O 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 μg/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 \times 10^4 times the initial Hg\(^0\) concentration, 45 μg/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\(_3\).

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\(_2\)SO\(_4\).\(^{17,18}\) 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).
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 Cl₂ in solution, turning its color from transparent into yellow. The concentration of Cl₂ is qualitatively proportional to the intensity of the color and qualitatively proportional to the absorption of light near a wavelength of 435 nm. In this study, 50 ppm of HCl in N₂ (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 Cl₂, 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 Cl₂ concentrations in the gas stream, where the relation between transmittances and Cl₂ concentrations was calibrated with a Cl₂ permeation tube (VICI Metronics). Although the concentration of Cl₂ 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 Hg⁰. Thus, Hg⁰ oxidation by Cl₂ can be expected in the PCD process, and some portion of Cl atoms can also contribute the Hg⁰ 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 Hg⁰ oxidation, where the Hg⁰ oxidation efficiency as a function of input energy density is obtained at four different HCl concentrations with NO 100 ppm and SO₂ 200 ppm. Higher concentration of HCl and input energy density result in more generation of Cl and Cl₂, and this gives rise to the better promotion of Hg⁰ oxidation to HgCl₂. Since the concentration 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 Hg⁰ even at low temperature.

In conclusion, Hg⁰ oxidation in the PCD process and the influence of two major pollutants, NO and SO₂, on this process have been investigated. Hg⁰ oxidation by O and O₃ can be viable, but it is seriously inhibited in the presence of NO due to the fast reaction of NO with O and O₃. On the other hand, SO₂ shows the little inhibitory effect on Hg⁰ oxidation due to the preferential reaction of SO₂ with OH rather than O and O₃. It was also observed that HCl in the PCD process can be dissociated into Cl and Cl₂ by energetic electrons and excited nitrogen species, and this induces the additional Hg⁰ oxidation to HgCl₂.

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