Behavior of mercury emitted from the combustion of coal and dried sewage sludge: The effect of unburned carbon, Cl, Cu and Fe

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A B S T R A C T

As the behavior of mercury generated from the combustion of mercury-containing fuels is highly dependent upon mercury speciation, many studies have investigated mercury speciation following combustion of various fuels. Unburned carbon and the content of chlorine (Cl), copper (Cu), and iron (Fe) compounds in ash are reported to affect the behavior of mercury. This study was conducted to understand the important factors impacting behavior of mercury from single coal combustion and co-combustion of dried sewage sludge with coal. Factors reported in previous studies were selected as potential factors affecting mercury oxidation and retention. Six coal and six dried sewage sludge samples were used to conduct single coal combustion and co-combustion tests. Each fuel sample was combusted in a lab-scale drop tube combustion system. Concentrations of elemental and oxidized mercury were determined using the Ontario Hydro Method. Ash samples collected on the bottom of the combustion system were analyzed to determine unburned carbon and mercury retention percentages. Unburned carbon and Cl were found to be important in both oxidation and retention of mercury for single coal combustion. Cl, Cu, and Fe content increased the oxidation of elemental mercury generated from co-combustion of dried sewage sludge with coal.

1. Introduction

Mercury is generated in flue gas following combustion of fuels containing mercury, such as fossil fuels and waste fuels. Three forms of mercury exist in the combustion flue gas: elemental, oxidized, and particulate. All of the gaseous mercury exists as elemental mercury under the high temperature in the furnace based on thermochemical equilibrium. The elemental mercury can be oxidized by subsequent cooling and homogeneous and heterogeneous reactions [1,2]. The amount of mercury controlled by conventional air pollution control devices is highly dependent upon mercury speciation [3,4]. Particulate mercury is easily captured by particulate matter control devices such as electrostatic precipitators (ESPs) and a fabric filter (FF) [3,5]. A significant amount of oxidized mercury can be captured by alkali and alkaline earth metal compounds used in a flue gas desulfurization (FGD) system [6]. However, elemental mercury captured by conventional air pollution control devices is negligible. Previous studies have reported that the formation mechanism of each mercury species is complex and affected by many factors. Gibb et al. [7] combusted four coal samples and investigated the fate of mercury generated by the combustion. They found that mercury retention in ash is closely related to the unburned carbon content of the ash. As unburned carbon content increased, mercury retention increased and gaseous mercury emission decreased. Wang et al. also reported that unburned carbon content is important for both oxidation and adsorption of mercury [8]. Results obtained from the analysis of fly ash collected in ESPs in pulverized bituminous coal-fired boilers also showed a consistent trend of increasing mercury retention with increasing unburned carbon content of ash [9]. However, Sable et al. found that mercury retention decreased with increasing unburned carbon content, implying that other factors also affect mercury capture on ash [10,11]. Chlorine content of fuel is reported to be closely related to oxidation of elemental mercury because the primary mercury oxidation product in flue gas is believed to be HgCl2 [9]. A study on the speciation of mercury in fly ashes using the temperature programmed decomposition technique reported that chlorine played an important role in mercury oxidation and retention [12,13]. In addition, ferric oxide (Fe2O3) and cupric oxide (CuO) in ash are reported to increase the oxidation of elemental mercury [14,15].

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Recently, energy conversion by combustion of dried sewage sludge has been suggested as a method to dispose of sewage sludge since the Ocean Dumping Act now regulates its disposal in the ocean. As dried sewage sludge has a heat value comparable to that of low rank coal, the co-combustion of dried sewage sludge with coal is one of the most promising methods for sewage sludge disposal. Sewage sludge is very different from coal in terms of mineral matter content, mercury content, and other properties. Due to these different properties, co-combustion of dried sewage sludge with coal may have different mercury emission behavior compared to the single combustion of coal. Studies have been conducted to understand mercury emission behavior from co-combustion of secondary fuel with coal. Tests were conducted on co-combustion of secondary fuels such as chicken manure, live residue, and wood with coal using a 50 kW entrained-flow pulverized combustion of secondary fuels such as chicken manure, live residue, and wood with coal. This was ascribed to the higher chlorine content of chicken manure, indicating the importance of chlorine in mercury oxidation.

Previous studies have reported that several factors such as unburned carbon, and metal and chlorine contents of fuel affect the behavior of mercury emitted from the combustion of solid fuels. However, only some of these factors were investigated in each study. To the best of our knowledge, this is the first study on the importance of each factor depending on the type of fuel being used. In addition, very few studies have been conducted to elucidate the behavior of mercury from co-combustion of dried sewage sludge with coal. In this study, concentrations of elemental and oxidized mercury were determined in the flue gas from single combustion of coal and co-combustion of dried sewage sludge with coal. The unburned carbon percentage, and the chlorine (Cl), copper (Cu), and iron (Fe) content of the fuel were selected as potential factors affecting the behavior of mercury. The effects of these factors on mercury oxidation and retention were investigated to gain a better understanding of the behavior of mercury from both single coal combustion and co-combustion of dried sewage sludge with coal.

2. Materials and method

2.1. Materials

Six coal and six dried sewage sludge samples were tested in this study. Two different ranks of coal samples with different compositions were used. Dried sewage sludge samples were obtained from different wastewater treatment plants. The samples were sieved to obtain the particles between 53 and 105 μm. Ultimate and proximate analyses of coal and dried sewage sludge samples were conducted, and the results are summarized in Table 1. The mercury content of each sample was determined using a solid mercury analyzer (DMA-80, Milestone, Inc., Shelton, CT, U.S.A.). Copper (Cu) and iron (Fe) content was determined using inductively coupled plasma optical emission spectroscopy (ICP-OES) techniques in order to investigate their effects on the oxidation of elemental mercury. Chlorine (Cl) content was determined using the oxygen bomb combustion-ion chromatography (EN 14582) method to use it as a potential factor in both oxidation and retention of mercury. Carbon (C) and mercury (Hg) content of the samples were used to determine post-combustion unburned carbon and mercury retention percentages, respectively. Proximate analysis of the samples was conducted using a thermogravimetric analyzer (Q600, TA Instruments Inc. U.S.A.). The higher heating values of the samples were determined using the Dulong's formula:

\[
H_h = 8100C + 34250(H - \frac{O}{8}) + 2250S \text{ kcal/kg fuel} \quad (1)
\]

where C, H, O and S are the content of carbon, hydrogen, oxygen and sulfur in weight mass fraction. As shown in Table 1, the metal content of dried sewage sludge samples is much higher than that of coal samples. Due to the very low ash content of coal sample B, the unburned carbon and mercury retention percentages were not determined for the ash from combustion of coal sample B. The mercury content of the dried sewage sludge samples is 10–40 times higher than that of the coal samples. As the sewage sludge samples were pre-dried using a specially designed heat-flow rotary kiln dryer, they have similar moisture content to the coal samples. For co-combustion, the coal sample A was selected because it has an average level of Cl, Cu and Fe content among the coal samples used in this study. Each dried sewage sludge sample was pre-mixed with the coal sample A at a mass ratio of 1:3 or 1:5. The coal sample F was also used in co-combustion tests for comparison purposes.

2.2. Experimental method

Experiments were conducted using a lab-scale combustion and gas analysis system as shown in Fig. 1. The system consists of three parts: (1) fuel feeding, (2) combustion, and (3) gas analysis. The feeder (Rovo feeder, Fine Techniques Co., Korea) is capable of precision feeding with high feed accuracy and constancy (repeatability 0.5%). Fuel was combusted in a drop tube furnace. The drop tube reactor was made of quartz, with an inside diameter of 4.4 cm. The drop tube reactor was covered by an electrical furnace with a height of 1 m. Three thermocouples were located outside the drop tube reactor along with the height of the furnace to control the temperature. The temperature outside the drop tube reactor was maintained at 950 °C i.e., above the auto-ignition temperature of the fuel. The combustion flue gas was analyzed using a gas analyzer (Vario Plus, MRU, Germany) and the Ontario Hydro Method. The gas analyzer determined the concentrations of carbon monoxide (CO) and carbon dioxide (CO2) in order to check the stability and extent of combustion. Mercury speciation was conducted using the Ontario Hydro Method. A heat tape with a temperature of 110 °C covered the reactor and tubing between the combustor and the impinger train to prevent water vapor from condensing on the inside of the reactor and tubing.

Each single and mixed fuel was combusted at an air/fuel ratio of 1.2. The injection rate of each fuel was determined in order to obtain the air/fuel ratio of 1.2 at an air flow rate of 4 L/min. Fuel was injected and burned at a constant rate in the drop tube furnace for 11 min. The combustion test conditions are summarized in Table 2. One stream of the sampled gas passed through the gas analyzer to measure concentrations of CO and CO2 every 2 s. The other stream of sampled gas passed through an impinger train containing a 1 N potassium chloride (KCl) solution and a 4 wt% potassium permanganate (KMnO4)/10 wt% sulfuric acid (H2SO4) solution. The concentration of oxidized mercury in the flue gas was determined from the amount of mercury absorbed in the KCl solution. The concentration of elemental mercury was determined using the Ontario Hydro Method. Based on the concentrations of oxidized ([Hg2+]out) and elemental ([Hg0]out) mercury, the mercury oxidation percentage was determined by the following equation:

Mercury oxidation(%) = \frac{[Hg^2+]_{out}}{[Hg^2+]_{out} + [Hg^0]_{out}} \times 100 \quad (2)
Ash leaving the furnace was collected on the bottom of the furnace and analyzed for the concentrations of unburned carbon and mercury. The unburned carbon concentration in the ash was determined by Korean standard loss on ignition (KS L 5405) method. The mercury concentration in the ash was determined using the solid mercury analyzer. Based on the unburned carbon ([C]_{ash}) and mercury ([Hg]_{ash}) concentrations in the ash, the unburned carbon and mercury retention percentages were determined by the following equations:

\[
\text{unburned carbon (\%)} = \frac{[C]_{ash}}{[C]_{sample}} \times \frac{[ash]_{sample} \times 100}{[C]_{2}}
\]

\[
\text{Mercury retention (\%)} = \frac{[Hg]_{ash}}{[Hg]_{sample}} \times \frac{[ash]_{sample} \times 100}{[C]_{2}}
\]

where \([C]_{sample}\), \([ash]_{sample}\) and \([Hg]_{sample}\) are the carbon, ash and mercury concentrations, respectively, in the sample. The unburned carbon percentage was estimated as loss on ignition because it has been reported to affect the behavior of mercury [15–17].

### 3. Results and discussion

#### 3.1. Combustion stability test

In addition to mercury speciation, combustion flue gas was analyzed for concentrations of CO and CO₂ to check the stability and extent of combustion. Fig. 2 shows the concentrations of CO and CO₂ in the flue gas generated from the combustion of coal A. As shown, the gas concentrations were consistent after approximately 1 min from the start of combustion. The average CO₂ concentration calculated after 1 min of combustion was more than 90% of the theoretical CO₂ concentration. The average CO concentration was as low as approximately 50 ppm. This suggests that combustion is stable and complete. The combustion flue gas was sampled for mercury speciation during 10 min after the first minute from the start of combustion, in order to obtain samples during stable and complete combustion. Stable and complete combustion was confirmed for all single combustion and co-combustion tests conducted in this study. Each combustion test under the same conditions was conducted four times, but only the results obtained under stable and complete combustion were used. Their average and standard error values were also determined to investigate the oxidation and retention of mercury with respect to the content of Cl, Cu and Fe.

#### 3.2. Single combustion of coal

Single coal combustion was conducted for six coal samples shown in Table 1. The concentrations of elemental and oxidized mercury in the flue gas generated from single coal combustion were determined, and mercury oxidation percentages were determined using Eq. (2). The results are presented in Figs. 3 and 4. As
shown in Fig. 3, different mercury emissions were found depending on the mercury content of the coal. Total mercury concentrations in the flue gas were found to be less than 3 μg/m^3 for all coal combustion tests. The mercury oxidation percentage in Fig. 4 shows a different trend of results from the total mercury concentration in Fig. 3. This suggests that mercury emission concentration is not related to the mercury oxidation percentage.

In order to identify the important factors affecting the oxidation of elemental mercury emitted from the single combustion of coal, the unburned carbon percentage was determined from the carbon concentration in ash obtained from each combustion test using Eq. (3). Fig. 5 presents the mercury oxidation percentage with the unburned carbon percentage. As shown, the mercury oxidation percentage is related to the unburned carbon and increases with an increase in the unburned carbon percentage. The mercury oxidation percentages of more than 30% located above the trend line are obtained from combustion of coal D and F which contain a high level of chlorine among the coal samples. In Fig. 6, the mercury oxidation percentage is presented with respect to the Cl, Cu, and Fe content of the coal samples. Chlorine content increases the oxidation of elemental mercury in flue gas as reported in several previous studies. However, Cu and Fe were found to have little effect on the oxidation of gaseous elemental mercury from single coal combustion.

The mercury retention percentage was also determined from the mercury concentration in ash obtained from each combustion test using Eq. (4). In Figs. 7 and 8 it is presented with respect to the unburned carbon percentage and Cl content, respectively, which were suggested as important factors in mercury oxidation. Similar to the mercury oxidation percentage, the mercury retention percentage increased in proportion to increases in the unburned carbon percentage and Cl content. Although Cl content showed closer relationship with mercury retention percentage than with mercury oxidation percentage, this may be ascribed that
the mercury retention percentage for the coal sample B was not determined due to its very low ash content. These results indicate that the unburned carbon percentage and Cl content are important in both oxidation and retention of mercury for single coal combustion. This also suggests that mercury oxidation is closely related to mercury retention for single coal combustion.

3.3. Co-combustion of dried sewage sludge with coal

Coal sample A was pre-mixed with each of the dried sewage sludge samples at a mass ratio of 3:1 or 5:1 and combusted. For this co-combustion, the outlet elemental and oxidized mercury concentrations, and the mercury oxidation, unburned carbon, and mercury retention percentages were determined as described for single coal combustion in the previous section. Fig. 9 shows the concentrations of elemental and oxidized mercury emitted from the co-combustion of dried sewage sludge with coal A compared to those from single combustion of coal A. As shown, gaseous mercury emissions significantly increased following co-combustion with the dried sludge samples. This is ascribed to the higher mercury content of the dried sewage sludge samples compared to that of the coal samples. In addition, higher mercury oxidation percentages were found in the co-combustion flue gases, compared to those in the combustion flue gas of coal A, as shown in Fig. 10. Similarly to single coal combustion, total mercury concentration was not related to the mercury oxidation percentage for the co-combustion.

Mercury oxidation percentages determined from each co-combustion test are presented with respect to the unburned carbon percentage in Fig. 11. In contrast to single coal combustion, unburned carbon was not related to the oxidation of gaseous elemental mercury from the co-combustion of dried sewage sludge with coal. Fig. 12 shows that Cu and Fe content, which were not factors in mercury oxidation for single coal combustion, affect

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![Fig. 6. Mercury oxidation percentage with Cl, Cu, and Fe content for single coal combustion.](image)

![Fig. 7. Mercury retention percentage with unburned carbon percentage for the single coal combustion.](image)

![Fig. 8. Mercury retention percentage with Cl content for single coal combustion.](image)

![Fig. 9. Concentrations of elemental and oxidized mercury in flue gas from co-combustion of dried sewage sludge with coal A.](image)
oxidation of elemental mercury from co-combustion. This may be ascribed to much higher Cu and Fe content of dried sewage sludge samples compared to coal samples. While unburned carbon and Cu and Fe content played differing roles in mercury oxidation between single coal combustion and co-combustion, Cl content played an important role in mercury oxidation for both single coal combustion and co-combustion, as shown in Fig. 12. To determine whether a potential confounding factor is associated, Cu and Fe content are presented in Fig. 13 with respect to Cl content. Cu and Fe content are closely related to Cl content, indicating that these are potential confounding factors. However, mercury oxidation percentages increased with co-combustion of dried sewage sludge compared to those obtained from single combustion of coal A, as shown in Fig. 10. In addition, co-combustion with dried sewage sludge samples 2 and 5, which have a lower Cl content than coal A, demonstrated higher mercury oxidation percentages than single combustion of coal A. This indicates that factors other than Cl content also affect oxidation of elemental mercury from co-combustion of dried sewage sludge. Due to more dominant effects of Cu and Fe on mercury oxidation, unburned carbon may have little effect on the oxidation of elemental mercury from the co-combustion.

Mercury retention percentages are presented with respect to the unburned carbon percentage and Cl content in Figs. 14 and 15, respectively. Fig. 14 shows that unburned carbon hardly affects mercury retention in co-combustion (similarly to mercury oxidation). Although Cl content increased mercury oxidation, it was not related to retention of mercury from co-combustion, as shown in Fig. 15. This may be ascribed to lower mercury retention percentages of 4.5–21.9% for co-combustion compared to 6.6–78.4% for single coal combustion. During co-combustion of dried sewage sludge with coal under our combustion test conditions, the oxidation of elemental mercury by Cl, Cu, and Fe compounds in ash may
be more dominant than retention of mercury on ash. However, in full-scale application, a significant amount of oxidized mercury generated from co-combustion may be captured onto fly ash in particulate matter control devices such as ESPs and an FF.

Among the factors affecting mercury oxidation and retention investigated in this study, Cl content was the only factor to affect the oxidation of elemental mercury from both single coal combustion and co-combustion. Fig. 16 presents the mercury oxidation percentage obtained from both combustion types with respect to fuel Cl content. Although Cl content was also shown to be somewhat related to oxidation of elemental mercury from both combustion types, co-combustion test results show a larger slope of increase in mercury oxidation with Cl content than those for the single coal combustion test. This indicates the increase in mercury oxidation is affected by other factors such as high Cu and Fe contents in ash from co-combustion of dried sewage sludge with coal. Additional co-combustion tests were conducted using coal F. Their mercury oxidation results are presented with respect to fuel Cl content in Fig. 17 in addition to the results from co-combustion of coal A. As shown in the figure, co-combustion test results of coal F show a similar trend of mercury oxidation results to those of coal A. This indicates that the behavior of mercury from co-combustion found in this study could be generally observed in the co-combustion of coal with dried sewage sludge. The effects of coal type and combustion condition on the behavior of mercury from co-combustion with dried sewage sludge will be investigated in future research.

4. Conclusion

Using a lab-scale drop tube combustion system, single combustion tests for six kinds of coal and co-combustion tests for six dried sewage sludge samples with coal were conducted. Concentrations of elemental and oxidized mercury emitted from each single coal combustion and co-combustion test were determined. To gain a better understanding of mercury emission behavior, mercury oxidation and retention percentages were determined after each combustion test. Unburned carbon percentage and Cl, Cu, and Fe content were selected as potential factors affecting mercury oxidation and retention. All factors investigated in this study were found to be potential factors affecting mercury oxidation during combustion. Important in mercury oxidation for single combustion of coal that contains a low level of metals, Cu and Fe content were important for mercury oxidation following co-combustion of coal and dried sewage sludge that contains large amounts of Cu and Fe. Cl content was found to be important for both single coal combustion and co-combustion. Co-combustion of dried sewage sludge with coal demonstrated higher gaseous mercury emissions and mercury oxidation percentages than single coal combustion. The higher mercury oxidation percentage may be ascribed to mercury oxidation by large amounts of Cu and Fe in ash, in addition to that by Cl. Unburned carbon and Cl content were also found to be important
factors in the retention of mercury from single coal combustion. Although the factors selected in this study were not found to be related to mercury retention for co-combustion, a significant amount of oxidized mercury generated from co-combustion may be captured onto fly ash in full-scale particulate matter control devices. Therefore, the content of Cl, Cu, and Fe, which affect mercury oxidation, may also be related to retention of mercury for co-combustion of dried sewage sludge with coal in full-scale operations. It is known that the oxidation of mercury can be facilitated through wall effects and by many surfaces [18–20], and the impact of the large surface-to-volume ratio of the small lab system [21,22] versus large commercial power plants will be investigated in future research. In addition, phosphorous is known to be an important constituent in sewage sludge [23], and the impact of phosphorous upon mercury speciation can be determined in future work.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.fuel.2017.04.104.

References


