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## SPECIATION OF MERCURY IN COAL AND SLUDGE COMBUSTION FLUE GASES

Because mercury has varying reactivity depending on its speciation, understanding mercury speciation is important in predicting the fates of mercury in combustion flue gases and formulating effective strategy of its control. Mercury speciation was determined in the combustion flue gases of coal and sludge. The extent of mercury oxidation was investigated with respect to changes in fuel properties and combustion conditions such as temperature and concentrations of oxygen (O<sub>2</sub>), carbon dioxide (CO<sub>2</sub>), carbon monoxide (CO), nitrogen oxides (NO<sub>x</sub>) and sulfur dioxide (SO<sub>2</sub>). Mercury content in the sludge samples was found to be much higher than that in the coal sample. O<sub>2</sub> and CO<sub>2</sub> concentrations were found to be closely related to Hg oxidation in the flue gases.

### 1. INTRODUCTION

Mercury (Hg) is known to have different fates in combustion flue gas depending on the fuel and combustion conditions and the configuration of air pollution control devices [1]. Three forms of mercury were found in the combustion flue gases of solid fuels: elemental mercury (Hg<sup>0</sup>), oxidized mercury (Hg<sup>2+</sup>) and particulate mercury (Hg<sup>p</sup>) [2]. Based on thermochemical equilibrium calculations at the temperatures typically produced when fuel is combusted in a furnace, mercury in the fuel may be generated in an elemental form as gaseous mercury. As the flue gas cools and interacts with other gases and fly ash, some of this elemental mercury is converted into oxidized forms. In addition, elemental mercury can be oxidized in a selective catalytic reduction (SCR) system designed to control nitrogen oxides (NO<sub>x</sub>) in flue gas [3, 4]. Because oxidized forms of mercury are highly water soluble and readily captured by alkali and alkaline earth metal compounds, significant amounts of oxidized mercury

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are reported to be captured in flue gas desulfurization (FGD) systems designed to control sulfur oxides ( $\text{SO}_x$ ) [5]. In addition, particulate mercury can be controlled by a particulate matter control device. However, elemental mercury is barely soluble in water and may not be captured in the existing devices installed for particulate control in combustion flue gas [6]. Therefore, determining the speciation of mercury in flue gas is a prerequisite for predicting the fate of mercury in the existing air pollution control devices and planning effective mercury control strategy. Mercury content in fuel varies with respect to fuel type. Chlorine content in fuel is reported to be closely related to the gas-phase oxidation of mercury in the flue gas because the formation of oxidized mercury involves the oxidation of elemental mercury by atomic chlorine (Cl) [1, 6, 7]. However, different from the effects of fuel properties on mercury oxidation, the effects of combustion conditions are not well understood.

Recently, energy conversion by combustion of various fuels such as biomass, sludge and waste has been suggested as a method to destroy their toxic constituents and to reduce the use of fossil fuels [8]. Because different fuels have different elemental compositions, combustion flue gases with differing constituents are expected with respect to the kind of fuel employed. It is therefore important to understand the constituents of flue gases from different fuels to apply effective controls for these gases. Compared to fossil fuels and waste, flue gases produced in the combustion of biomass and sludge have not been well investigated and are not understood. In particular, very few studies have investigated the mercury content in those fuels or mercury speciation in their combustion flue gases. We therefore analyzed coal, woodchip and sludge for their elemental contents including mercury. These fuels were combusted in a bench-scale furnace, and mercury speciation was conducted in their flue gases. The speciation results were also investigated as a function of combustion conditions.

## 2. EXPERIMENTAL

*Fuel.* Pulverized coal, woodchip and sludge samples were prepared for this study. Table 1 shows the results obtained from elemental analysis of the samples. Although detailed information regarding a pulverized coal sample was not available, the sample was not considered to be anthracite, judging from its low carbon content. Woodchips were obtained from a local saw mill. Sludge samples were obtained from two locations: a steel mill (A) and a sewage treatment plant (B). As shown in the table, the sludge B sample had much higher chlorine content than the sludge A sample. The mercury content in the samples was also determined using a DMA-80 direct mercury analyzer (Milestone Inc. Shelton, CT, USA). After each sample was introduced into the analyzer, the sample was dried and combusted. Mercury vapor in the combustion gas was then collected on a gold amalgamation trap, the collected mercury vapor was desorbed, and the desorbed mercury was detected by the atomic absorption spectrometry.

Table 1. Elemental compositions of the solid fuel samples

Sample	Carbon [%]	Hydrogen [%]	Sulfur [%]	Oxygen [%]	Chlorine [ppm]	Mercury [ppb]	Chlorine/mercury [ppm/ppb]
Coal	67.2	4.1	< 0.01	11.2	26.0	12	2.2
Woodchip	38.0	4.5	< 0.01	32.4	36.5	<5	> 7.3
Sludge A	27.2	4.3	0.6	21.5	138.4	920	0.15
Sludge B	33.0	5.4	1.1	22.6	9571.5	1200	8.0

The mercury contents in both sludge samples were determined to be much higher than those in woodchips and coal. Mercury concentrations in the combustion flue gases of sludge were therefore expected to be much higher than those in other fuels. Because a very small amount of mercury was found in the woodchip sample, its combustion was not analyzed in this study. The coal sample had a relatively lower level of mercury than most coal samples, which have generally been reported to have an average mercury concentration of approximately 100 ppb [1, 2]. The sludge samples were dried and ground using a ball mill and then sieved through a screen; particles below 250  $\mu\text{m}$  were used for the combustion tests.

*Combustion of solid fuels and analysis of flue gases.* The sludge and coal samples were combusted in a bench-scale furnace. A schematic diagram of the furnace and gas sampling system is shown in Fig. 1.

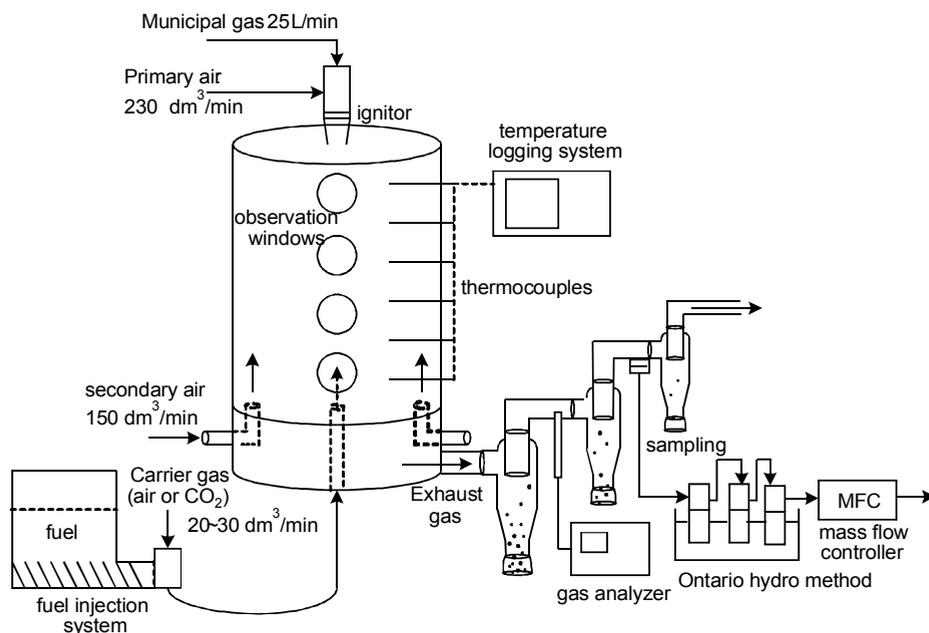


Fig. 1. Schematic diagram of the experimental system

Municipal gas (composed of approximately 90% methane) was introduced into the furnace and burned in air until the temperature increased to approximately 900 °C. Six thermocouples were placed inside the furnace along its height, and the temperatures were monitored and recorded using a temperature logging system (GL450 midi logger, GRAPHTEC Corp., Yokohama, Japan). The combustion flame was also observed through observation windows. Each fuel was then introduced into the furnace via a fuel injection system. A screw-type feeder was installed in the fuel injection system to provide solid fuel at a constant rate of 1 kg/h. Air or carbon dioxide (CO<sub>2</sub>) was used as a carrier gas to study the effect of combustion environment on mercury speciation in the flue gas. Each fuel was combusted in the temperature range of 850–950 °C. To ensure complete combustion of the solid fuels in the bench-scale furnace, the air/fuel ratio was maintained in the range of 1.2–1.4 depending on the kind of fuel and carrier gas. The flow rates of municipal gas, air and solid fuel are also shown in Fig. 1.

A series of cyclones were connected to the furnace to separate particles from the exhaust gas. An analyzing sensor was located in the exhaust gas stream, and concentrations of oxygen (O<sub>2</sub>), CO<sub>2</sub>, carbon monoxide (CO), NO<sub>x</sub> and sulfur dioxide (SO<sub>2</sub>) were monitored and recorded using a gas analyzer (Vario Plus Industrial, MRU Instruments Inc., Germany) In particular, CO concentration was monitored to verify complete combustion, and the flow rate of air was controlled depending on the CO concentration. A portion of the combustion flue gas was sampled at a flow rate of 2 dm<sup>3</sup>/min to determine the concentrations of elemental and oxidized mercury in the flue gas. The Ontario hydro method [9] was used to speciate mercury; a 1 M KCl impinger solution and a 4% (w/v) KMnO<sub>4</sub>/10% (v/v) H<sub>2</sub>SO<sub>4</sub> impinger solution were located, as shown in Fig. 1, to capture oxidized mercury and elemental mercury in the sampled gas, respectively. The oxidized mercury (Hg<sub>gas</sub><sup>2+</sup>) and elemental mercury (Hg<sub>gas</sub><sup>0</sup>) concentrations in the combustion flue gas were then determined by analyzing those solutions using the mercury analyzer. Each test was conducted for 20 min. The concentrations of O<sub>2</sub>, CO<sub>2</sub>, CO, NO<sub>x</sub> and SO<sub>2</sub> in the flue gas were recorded every 2 s using the gas analyzer, and the concentrations of mercury species in the flue gas were determined from the analysis of the impinger solutions after sampling.

### 3. RESULTS AND DISCUSSION

#### 3.1. SPECIATION OF MERCURY IN THE COMBUSTION FLUE GASES OF SOLID FUELS

Mercury speciation was conducted for the flue gases generated from the combustion of coal and sludge samples as described in the Experimental section. Figure 2 shows elemental and oxidized mercury concentrations corrected to 4% O<sub>2</sub> in the flue gases determined after each test. As shown in the figure, the sludge A and B samples

show much higher levels of mercury emissions than the coal sample. This is attributed to higher mercury content in the sludge samples as shown in Table 1. This result suggests that the effective control of mercury will be necessary in a combustion process using sludge.

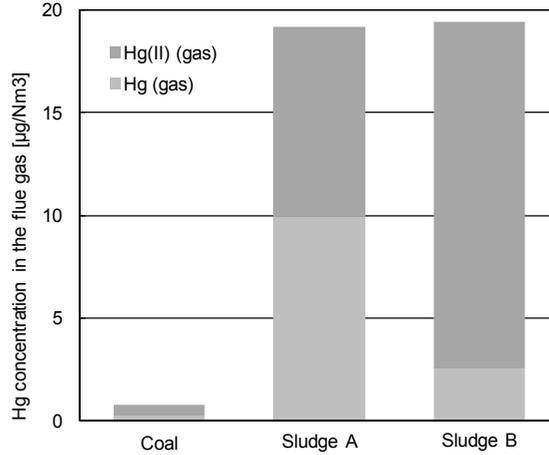


Fig. 2. Elemental and oxidized mercury concentrations corrected to 4% O<sub>2</sub> in the flue gas from the combustion of each fuel sample carried by air

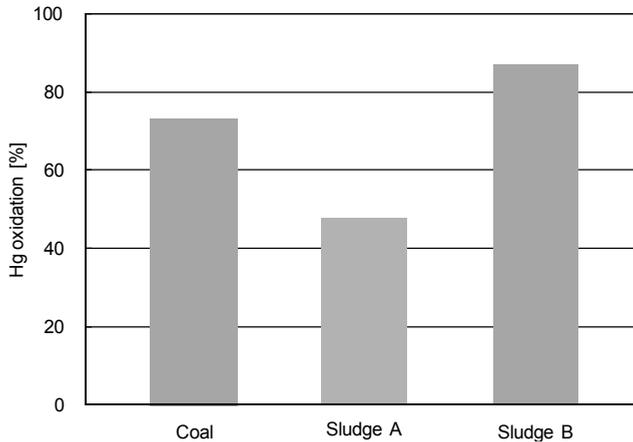


Fig. 3. Oxidation percentage of mercury in the combustion gases of coal and sludge fuel samples carried by air

Based on the elemental and oxidized mercury concentrations, the mercury oxidation percentage was calculated by the following equation to determine the quantity of mercury oxidized in the combustion flue gas as a function of fuel properties and combustion conditions:

$$\text{Hg oxidation} = \frac{[\text{Hg}_{\text{gas}}^{2+}]}{[\text{Hg}_{\text{gas}}^0] + [\text{Hg}_{\text{gas}}^{2+}]} \times 100\%$$

Figure 3 shows the mercury oxidation percentages in the combustion gases of coal, sludge A and sludge B. Sludge B, which had the highest chlorine content, showed the highest mercury oxidation percentage. As reported in previous studies [1, 6, 7], the chlorine content of in fuel influences the oxidation of mercury in the flue gases. However, although our coal had lower chlorine content than sludge A, it showed a higher mercury oxidation percentage than sludge A. This may be ascribed to the lower ratio of chlorine content to mercury content in the coal. This result suggests that the ratio of chlorine content to mercury content in fuel is an important factor in Hg oxidation when the mercury content in a fuel is relatively low.

### 3.2. EFFECTS OF O<sub>2</sub> AND CO<sub>2</sub> CONCENTRATIONS ON Hg OXIDATION DURING COMBUSTION

Compared to the effects of the fuel properties on Hg oxidation, the effects of combustion conditions are less well understood. Although the hydrogen chloride (HCl) concentration in flue gas is reported to play an important role in Hg oxidation [2, 7, 10], the effects of other combustion gases have not been investigated. Hence, the data for concentrations of O<sub>2</sub>, CO<sub>2</sub>, CO, NO<sub>x</sub> and SO<sub>2</sub> and combustion temperatures recorded during the tests were averaged to investigate Hg oxidation with respect to each combustion condition. As a result, CO, NO<sub>x</sub> and SO<sub>2</sub> concentrations in the flue gas and the combustion temperature were not found to be closely related to mercury oxidation in the flue gas.

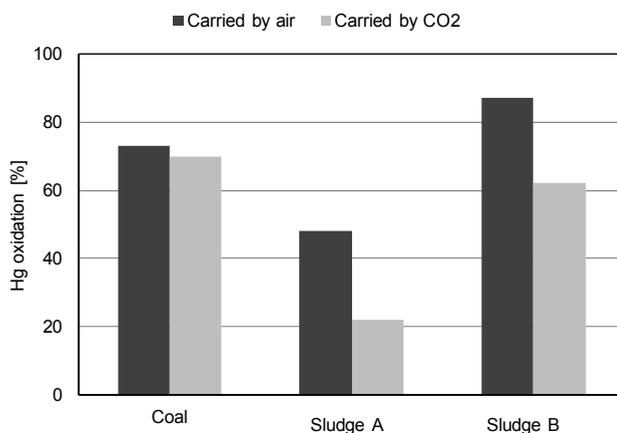


Fig. 4. Hg oxidation percentage in the combustion flue gases of coal, sludge A and sludge B carried by air and CO<sub>2</sub>

Further tests were conducted to investigate the effect of CO<sub>2</sub> concentration on mercury oxidation. CO<sub>2</sub> was used as a carrier gas instead of air for the fuel injection to create a more CO<sub>2</sub> rich combustion environment. Figure 4 shows the Hg oxidation percentages in the combustion flue gases of solid fuels carried by air and CO<sub>2</sub>. As shown here, Hg oxidation generally decreased when the fuel was carried by CO<sub>2</sub>.

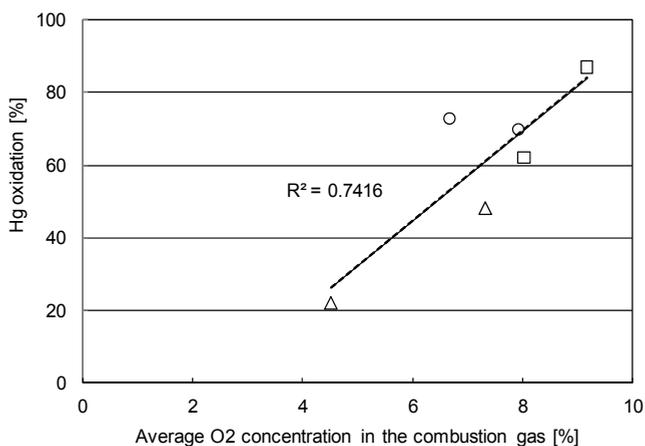


Fig. 5. Hg oxidation percentage with respect to the average O<sub>2</sub> concentration for the combustion of tested fuels (circular markers for coal, triangular markers for sludge A and rectangular markers for sludge B)

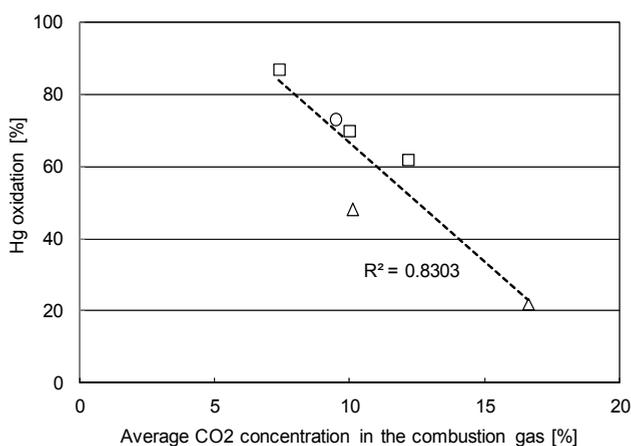


Fig. 6. Hg oxidation percentage with respect to the average CO<sub>2</sub> concentration for the combustion of tested fuels (circular markers for coal, triangular markers for sludge A and rectangular markers for sludge B)

In Figures 5 and 6, Hg oxidation percentages are presented as functions of the average O<sub>2</sub> concentration and the average CO<sub>2</sub> concentration, respectively, for the com-

bustion of all tested fuels. The data trend lines were determined for all the tested fuels, i.e., coal, sludge A and sludge B, and the coefficients of determination ( $R^2$ ) were calculated. As shown in Figs. 5 and 6, Hg oxidation generally increased with an increase in  $O_2$  concentration and decreased with an increase in  $CO_2$  concentration, regardless of the fuel type. Based on these results, it is unclear which gas concentration is a more dominant factor in Hg oxidation because the  $O_2$  concentration varied inversely proportionally to the  $CO_2$  concentration during these combustion tests. However, the experimental results suggest that the  $O_2$  and  $CO_2$  concentrations during combustion also affect Hg oxidation in the flue gases of solid fuels.

#### 4. CONCLUSIONS

Coal and sludge were combusted in a bench-scale furnace, and the concentrations of mercury and several gases in the flue gas were measured to study mercury oxidation with respect to the fuel properties and combustion conditions. In addition to the chlorine content in the fuel, the ratio of chlorine to mercury contents appeared to be an important factor in Hg oxidation in the combustion flue gas of coal, which has a lower mercury content than sludge. Combustion temperature and CO,  $NO_x$  and  $SO_2$  concentrations were not found to be important factors in Hg oxidation. Although it was unclear from the test results whether the  $O_2$  or  $CO_2$  concentration was the more dominant factor for Hg oxidation, Hg oxidation was found to be enhanced by an increase in  $O_2$  concentration and reduced by an increase in  $CO_2$  concentration. This indicates that mercury speciation in an air combustion flue gas may be different from that in the oxy-combustion flue gas for the same fuel. In addition to the increased  $CO_2$  concentration of the oxy-combustion flue gas, oxy-combustion is conducted with an increased  $O_2$  concentration compared to air combustion. Therefore, mercury speciation in an oxy-combustion flue gases may be better understood by the quantitative study of the relationships between Hg oxidation and  $O_2$  and  $CO_2$  concentrations in combustion gases.

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