An Investigation of Mercury Emission from FBC Systems Fired with High-Chlorine Coals

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Mercury is widely used in industry because of its diverse properties, which makes it an important part of industrial processes and an important ingredient in many products. However, concern over health issues has led to a 75% decline in industrial demand for mercury over the past 11 years. The objective of this project was to study the reduction of mercury emission from coal-fired combustors by using HCl provided by high-chlorine coals to help convert elemental mercury to oxidized mercury at relatively low temperatures (500–600 °C). By oxidizing elemental mercury inside a fluidized bed combustion (FBC) system, total mercury emissions can be reduced with high efficiency and low cost while maintaining low emissions of other pollutants. The results of the study indicate that using high-chlorine coal in an FBC system converted more than 99% of elemental mercury to an oxidized state, mainly HgCl₂. Without secondary air injection and after cooling the flue gas to 400 °C by using a convective heat exchange tube bank, the typical concentration of gas-phase mercury in FBC flue gas was 1500–3000 ng/Nm³ flue gas. Better results were obtained by using high-chlorine coals and a predetermined ratio of secondary air (secondary/primary air ratio > 0.15). Only 0.5% of the total mercury input was emitted from the combustor in the elemental form. When a high-chlorine coal was used, close to 55% of the total mercury input was found in the solid phase (bed and fly ash). Of the mercury found in the solid phase, almost none was found in the bed ash because of its high surrounding temperature (850 °C). The gas-phase mercury, which was around 45% of the total mercury input, was determined to be primarily in the oxidized state (40% of the total mercury input), while only a small portion (4.5% of total mercury input) still existed as elemental mercury in the flue gas even when a high-chlorine (0.42 wt %) coal was burned without the benefit of secondary air injection. Our experimental results indicate that the combustion temperature and secondary/primary air ratio are two major factors that influence mercury emissions in an FBC system when limestone is used as sorbent.

Introduction

On the basis of the available evidence on health effects, the U.S. Environmental Protection Agency (EPA) has been evaluating the need to regulate mercury releases into the environment. In response to the Congressional mandates in the Clean Air Act Amendments of 1990, EPA issued the Mercury Study Report and the Study of Hazardous Air Pollutant Emissions from Electric Utility Steam Generating Units Report. Despite the enormous effort represented by these reports, as well as the efforts of both DOE and EPRI in conducting the field measurement programs which aided in forming the basis for these reports, a definitive answer on the need for mercury regulation has not been found. However, EPA, as well as other regulatory agencies and health researchers, has suggested a “plausible link” between anthropogenic sources emitting mercury and mercury methylation, bioaccumulation in the food chain, and adverse health effects in humans and wildlife.1

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Mercury exists in three forms, elemental mercury, inorganic mercury compounds, and organic mercury compounds, with each form of mercury having a very different exposure potential. Oxidized mercury is soluble and has a tendency to associate with particulate matter. Therefore, emissions of oxidized mercury may be efficiently controlled by air emission and particulate controlling apparatuses such as flue gas desulfurization (FGD) systems or particulate precipitators or activated particulate with precipitators. A recent study indicated particulate control devices (PCDs) remove particulate-bound mercury efficiently, fabric filters (FFs) remove an average of 73% of gaseous mercury and FGDs remove oxidized mercury with an efficiency of about 90%, as do spray dryer absorbers (SDAs). Any oxidized mercury that is not captured by fly ash, an activated particulate, or FGD system is deposited on a local or regional scale, thus limiting its environmental impact. On the other hand, elemental mercury is extremely volatile and insoluble. Elemental mercury has a high vapor pressure at the operating temperatures of typical air emission and particulate control devices. Therefore, effective collection by particulate matter control devices is highly variable. Also, elemental mercury is not captured by FGD and any kind of PCDs systems. While elemental mercury may be removed by some chemically treated activated carbon or selective absorbents, they are more difficult to collect and treat. In contrast to oxidized mercury, elemental mercury travels hundreds of kilometers and contributes to the increasing atmospheric load. Therefore, elemental mercury emissions are harder to reduce than oxidized mercury emissions and have an environmental impact over a larger area.

Mercury emissions from coal-fired power plants have been extensively evaluated for nearly 10 years to aid in determining possible regulation by EPA. EPA has indicated 51.6 tons of mercury are emitted annually as a result of coal utilization in the utility industry. Assuming a 30% boiler efficiency (converting thermal energy to electricity) and operation at 70% of full load (including downtime), an estimated 45 tons of mercury are emitted to the atmosphere by coal utilities in the United States. Considerable effort has gone into developing possible efficient, low-cost technologies for mercury emission reductions from utility plants. The goal of the Department of Energy’s Mercury Measurement and Control Program is to develop control strategies for reducing the current annual utility mercury emissions by 50 to 70% by 2005 and by 90% by 2010 at a cost between one-quarter to one-half of the current cost estimates.

More recent studies indicate that the distribution of Hg species in coal-fired flue gas is strongly dependent on the type of coal (e.g., bituminous, subbituminous, or lignite), the operating conditions of the combustion system (in terms of unburned carbon in the ash), and temperature and residence time in the particulate control device. The variability in the distribution of vapor-phase mercury species in coal-fired flue gas may depend on the coal’s chloride concentration. It has been observed that higher concentrations of ionic mercury are obtained in utility flue gas when the combusted coal has a high chloride content (0.1 to 0.3 wt %). Based on the data collected from EPA’s information collection request (ICR), the threshold concentration for mercury conversion from elemental to an ionic form is 200 ppm. Furthermore, other components of the air pollutant control system, such as FGD and SCR systems, have also been shown to affect both the speciation of mercury in the stack and the amount of mercury removed in the air pollutant control equipment.

It has been speculated that the oxidized form of Hg in flue gas from coal combustion is mercuric chloride (HgCl₂). The existence of molecular chlorine at temperatures measured near the first air pollutant control devices (APCD) of coal-fired power plants has been postulated. Kinetic calculations also showed that the chlorine atoms combine to form primarily HCl with...
minor amounts of \( \text{Cl}_2 \). If small concentrations of \( \text{Cl}_2 \) are present in the flue gas streams exiting the air preheater, then reactions could be occurring with the \( \text{Hg}^0 \) to subsequently form \( \text{HgCl}_2 \). Consideration of the elementary reaction of mercury in flue gas has led several groups to conclude that the reaction of \( \text{Hg}^0 \) and atomic chlorine (Cl) in the flue gas initiates the conversion to \( \text{HgCl}_2 \). Since molecular chlorine is formed by the reaction of atomic chlorine, the presence of \( \text{Cl}_2 \) in the flue gas is a possible indication of the presence of atomic chlorine. Alternatively, mercury could react with other vapor-phase compounds and/or fly ash constituents to form other oxidized mercury compounds.\(^{18,19}\)

The objective of this project was to study the reduction of mercury emission from coal-fired combustors by using HCl provided by the combustion of high-chlorine coals to help convert elemental mercury to oxidized mercury at relatively low temperatures (500–600 °C). By oxidizing elemental mercury inside the fluidized-bed combustion (FBC) system, total mercury emissions can be reduced with high efficiency and low cost while maintaining low emissions of other pollutants.

**Experimental Section**

A thermogravimetric analyzer (TGA) was used to follow the release of mercury during the coal pyrolysis and combustion processes. The WKU 0.1 MWth (MWth, thermal input) FBC system was utilized to conduct the study of mercury emissions produced during coal combustion processes. In the TGA study, the study focused on the effect of final temperature and surrounding atmosphere on the mercury released. During the FBC combustion test, the effect of coal types, surrounding temperature, and secondary/primary air ratios on mercury emissions were investigated.

**TGA Study.** Samples Used. A bituminous coal (WKU 99626) was used in this study to investigate the effect of chlorine and sulfur contents on mercury emission. Five blends, with Ca/S molar ratios of 1, 1.5, 2, 2.5, and 3, were tested to study the effect of limestone addition on mercury retention by combustion residues.

Experimental Methods. A TA Instruments thermogravimetric analyzer (TA 951), was heated to the desired temperature using a "jump" (rapid ramp) method. In each test run a period of 20 min was used to allow the TGA to reach the desired value. The sample, approximately 1.2 g, was placed in a ceramic boat and then loaded into the TGA furnace. Two atmospheres were selected. Nitrogen was used to simulate the coal pyrolysis process and air was used to simulate coal combustion conditions. The residues from the pyrolysis and combustion processes were collected and analyzed. The differences between the mercury contents in original samples and the residues represent the mercury released into the flue gases.

**WKU 0.1 MWth Fluidized Bed Combustor (FBC).** The bench-scale 0.1 MWth fluidized bed combustor (FBC) at Western Kentucky University (WKU) was used in this study. Figure 1 is a schematic diagram of the system, which has a 0.3 m I.D. and 3.5 m height, and was designed to serve as a flexible research and development facility. The combustor's operating parameters (air/water flow, coal/lime feed rate, bunker weight, temperatures, and pressure) are controlled by a computer. During combustion runs any needed changes in the parameters can easily be entered into the computer by accessing the correct control screen and making the necessary corrections on line. To improve combustion and reduce pollutant emissions, two sets of secondary air nozzles were installed in the combustor. The first set of secondary air ports, fitted with two nozzles, is 1.6 m above the setter plate and the second set is 0.6 m above the first one. Forced air, at a calculated ratio, is injected tangentially at an angle of 30° into the freeboard through secondary air nozzles. This air forms a

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strong vortex flow above the nozzles. Under this tangential flow, particles escaping from the fluidized bed are separated from the flow. The large particles fall back into the bed along the wall, while the small particles form a suspended layer to prolong their residence time in the combustor.

A Shimadzu GC-8A gas chromatograph was used to continuously monitor the oxygen, carbon monoxide, and hydrogen chloride concentrations in the flue gas during the 1000-h runs. The results were used to adjust the coal and limestone feeding rates and the combustion air supply flow rate. An infrared absorption-based photoacoustic multi-gas analyzer (INNOVA 1312) was used to measure carbon dioxide, moisture, and sulfur dioxide concentrations. The measurement errors are 0.1 ppm for SO₂ and HCl; 1 ppm for CO; and 0.1% for H₂O, CO₂, and O₂. These three instruments were calibrated with standard gases twice each day.

The Ontario Hydro Method was chosen for mercury sampling during all tests. A LECO Advanced Mercury Analyzer (Model AMA-254) was used in this study. In the Ontario Hydro Method, flue gas is pulled by a vacuum through a series of impingers containing three different absorbing solutions: KMnO₄/H₂SO₄, HNO₃/H₂O₂, and KCl. The KMnO₄/H₂SO₄ and HNO₃/H₂O₂ solutions collect elemental mercury, Hg⁰. The KCl solution collects oxidized mercury, Hg⁺, and methylmercury. Additionally, a filter is placed before the impingers to collect particulate mercury, which may be present in the flue gas. In addition to using the absorbing solutions to collect mercury, the Ontario Hydro Method uses an ice bath to lower the flue gas temperature below the boiling point of mercury. After sampling, solutions were analyzed using a LECO AMA-254 mercury analysis system. The KCl trap solution was extracted with methylene chloride to recover methylmercury. In the LECO AMA-254 Advanced Mercury Analyzer, the sample boat is automatically inserted into a quartz decomposition tube, which is heated by two independent furnaces, the dry/ decomposition furnace and catalyst furnace. Within the decomposition tube, the sample is first dried and then thermally decomposed. A flow of oxygen carries the decomposition products into the catalyst core, where the decomposition is completed at a temperature of 750 °C and acidic halides and oxides are trapped. The remaining products are carried to the gold amalgamator that selectively traps mercury. The amalgamator is then rapidly heated, releasing the mercury vapor into the dual range absorbance cuvettes. In the absorbance cuvettes, mercury content is measured as a function of peak heights at 253.65 nm by a silicon diode UV detector. The AMA-254 has a 0.01 ng Hg detection limit (0.01 ng refers to the amount of Hg in the measuring cuvette of the AMA-254), a working range from 0.05 to 600 ng, a reproducibility smaller than 1.5% and requires five minutes for analysis.

Five combustion tests were carried out firing four kinds of coal and one blend fuel. The analytical values for the four test coals are given in Table 1. The analytical parameters for the four test coals are very similar, except for the sulfur and chlorine contents.

### Results and Discussions

#### Mercury Release Performance in TGA Experiments

In the thermogravimetric heating curve for coal in nitrogen and in air, as shown in Figure 2, the peak labeled I at around 100 °C was due to the loss of inherent moisture, and the major decomposition peak labeled II at about 440 °C is the result of volatile matter release. The volatile matter evolved includes water, CO, CO₂, SO₂, HCl, as well as aliphatic and aromatic fragments. In a nitrogen atmosphere the coal sample maintained a relatively constant mass-loss rate until 850 °C. In an air atmosphere the multiple peak, II, was due to overlapping reactions (oxidative devolatilization and combustion). It is difficult to identify mercury in the gas species using TG-FTIR or TG-MS techniques during the dynamic TGA run.

#### Temperature Effect

Mercury emission from coal is very sensitive to temperature, as has been reported in several studies. All types of mercury (both inorganic and organic) can be released completely after decomposition to the elemental mercury form when the temperature is higher than 650 °C. Figure 3 illustrates the mercury release results under a series of final temperatures in two atmospheres. The solid line represents the data obtained in a nitrogen atmosphere that was used to simulate the coal pyrolysis process. The dashed line represents the results collected using an air atmosphere to simulate a coal combustion process. The curve shows that there are two major steps for mercury emission during pyrolysis. The first step is emission of free mercury compounds (Hg⁰ and ionic mercury, such as Hg₂⁺) at temperatures lower than 350 °C. This assumption is consistent with the data from experiments involving the pyrolysis of pyrite, where the only mercury released occurred around 350 °C. Nearly 35% of the total mercury in the coal was released during this process. The second step is emission of organic mercury (linked or bonded to organic compounds of coal) during the devolatilization process. A large portion (60%) of the total mercury in coal 99626 was released in the temperature range of 350–400 °C. The results for mercury emission during combustion were very different from those obtained during pyrolysis. During combustion, the mercury was almost completely released before the devolatilization temperature and 96% of the total mercury in the coal was emitted when the final temperature had reached 300 °C. These results indicate that oxygen accelerates the breaking of linkages and bonds between mercury and organic compounds.

#### Limestone Effect

The effect of limestone addition on the amount of mercury released was investigated and the results are shown in Figure 4. From Figure 4, there is no marked change in the mercury release curve obtained in an air atmosphere with the Ca/S molar ratio

| Table 1. Analytical Valuesa for the Coals Used in the Study |
|---|---|---|---|---|
| 97025 | 98111 | 99426 | 99626 |
| % moisture | 4.56 | 10.25 | 2.33 | 6.96 |
| % ash | 10.97 | 9.67 | 8.70 | 13.81 |
| % volatile matter | 36.25 | 34.84 | 36.98 | 34.14 |
| % fixed carbon | 52.78 | 55.49 | 54.32 | 52.05 |

a Moisture is as-received, all other values are reported on a dry basis.

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Liu et al.
in the range of 0 to 3. However, for the pyrolysis process, the percent of total mercury released from the coal was reduced to 88.8% from 99.3% when Ca/S molar ratio was increased from 0 to 3. The results indicate that limestone addition may inhibit mercury emission during coal pyrolysis.

**Mercury Emission Performance in an FBC System.** Five combustion tests were carried out firing four coals (Table 1) and one blend of WKU Coal 97025 with 1% PVC. Typical emission levels of HCl and SO$_x$ for the five runs are listed in Table 2. The test conditions were essentially the same for all five runs. Flue gas derived from the blend fuel (coal 97025 with 1% PVC) had the highest HCl concentration (75.7 ppm), followed by coal 98111 (55.3 ppm), coal 99626 (55.1 ppm), coal 97025 (44.3 ppm), and coal 99426 (2.8 ppm). For other flue gas components, including O$_2$, CO, and NO, the concentrations are in a narrow range (CO $\sim$ 110–210 ppm, O$_2$ $\sim$ 4.5–5.0%, NO $\sim$ 300–350 ppm). The concentration of water vapor in the five flue gases covers a wide range, from 4.2% (coal 97025) to 7.27% (coal 99626). A previous study$^{20}$ reported that moisture in the flue gas has a significant influence on mercury sorption by being involved in the SO$_2$$-$NO$_2$ interaction. However, the study also indicated the critical concentration of moisture is very low, less than 0.5%.

The Effect of Coal Type. Evidence from studies conducted on pilot- and full-scale combustion systems is not consistent with the assumption of equilibrium for Hg species in flue gas at the temperatures (nominal 149 °C) corresponding to the location of the air pollutant control devices (APCD). At the inlet to the first APCD, measurements taken using the Ontario Hydro Mercury Speciation Method (Ontario Hydro Method) in both pilot- and full-scale combustion systems indicate a wide range of Hg$^{2+}$ percentages while firing coals of various ranks:$^{21-26}$ (1) bituminous coal with Hg$^{2+}$ values from 70 to 88%; (2) Powder River Basin (PRB)/subbituminous coal.

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coal with \( \text{Hg}^{2+} \) values from 15 to 50% and; and (3) lignite coals with highly variable \( \text{Hg}^{2+} \) values ranging from 10 to 30%, but as high as 50%.

Bituminous coals have the highest chlorine concentrations in the range of 500–1300 ppmw, with 50–130 ppmw of \( \text{HCl} \) measured in the flue gas. As observed, the \( \text{Hg}^{2+} \) percentages are the highest in the flue gas from these coals. Lignite has some of the lowest measured concentrations, from nondetected to 60 ppmw, with corresponding \( \text{HCl} \) measured concentration in the flue gas ranging from nondetected to 2 ppmw. Flue gas from the combustion of lignite coal contains a corresponding low \( \text{Hg}^{2+} \) percentage. PRB/subbituminous coals also yield low concentrations of \( \text{Hg}^{2+} \) in the flue gas while also having low chlorine concentrations, from nondetected to 60 ppmw. This corresponds to \( \text{HCl} \) concentrations measured in the flue gas from nondetected to ~5 ppmw. Several studies have indicated the chlorine content in the coal shows the same effect on mercury emission in FBC systems as that in the pulverized combustion systems.

Two coals with different chlorine contents (coal 97025 and 99426) and one blend fuel (coal 97025 blended with 1% PVC) were tested in the WKU FBC system. Figure 5 illustrates the effect of coal chlorine content on mercury emissions. The data indicate that the total amount of gas-phase mercury is reduced significantly with an increase in the chlorine content in coal, from

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**Table 2. Summary of Steady-State Run Conditions**

<table>
<thead>
<tr>
<th>Condition</th>
<th>coal 97025</th>
<th>coal 97025 + 1% PVC</th>
<th>coal 98111</th>
<th>coal 99426</th>
<th>coal 99626</th>
</tr>
</thead>
<tbody>
<tr>
<td>fuel feed rate (kg/h)</td>
<td>7.50</td>
<td>7.95</td>
<td>8.21</td>
<td>8.16</td>
<td>7.26</td>
</tr>
<tr>
<td>limestone feed rate (kg/h)</td>
<td>1.71</td>
<td>1.82</td>
<td>1.43</td>
<td>2.02</td>
<td>3.22</td>
</tr>
<tr>
<td>bed temperature (K)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>at 0.56 m</td>
<td>1113</td>
<td>1173</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>at 0.97 m</td>
<td>1108</td>
<td>1168</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>at 1.50 m</td>
<td>1073</td>
<td>1133</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>at 2.60 m</td>
<td>958</td>
<td>1023</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>at 3.30 m</td>
<td>843</td>
<td>923</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{SO}_2 ) concentration (ppm)</td>
<td>245</td>
<td>194</td>
<td>114</td>
<td>53</td>
<td>282</td>
</tr>
<tr>
<td>( \text{HCl} ) concentration (ppm)</td>
<td>44.3</td>
<td>75.7</td>
<td>55.3</td>
<td>2.8</td>
<td>55.1</td>
</tr>
<tr>
<td>( \text{O}_2 ) concentration (vol %)</td>
<td>4.7</td>
<td>4.5</td>
<td>5.02</td>
<td>4.71</td>
<td>4.79</td>
</tr>
<tr>
<td>( \text{CO} ) concentration (ppm)</td>
<td>156</td>
<td>214</td>
<td>156</td>
<td>113</td>
<td>173</td>
</tr>
<tr>
<td>moisture concentration (vol %)</td>
<td>4.21</td>
<td>4.51</td>
<td>4.24</td>
<td>5.13</td>
<td>7.27</td>
</tr>
</tbody>
</table>

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**Figure 5.** The effect of coal chlorine content on mercury emissions in flue gas.

64.3% for coal 99426 (Cl = 0.026%), to 54.3% for coal 97025 (Cl = 0.21%), and 48.2% for the blend fuel (coal 97025 with 1% PVC). The major differences between mercury emission for coal 99426 and coal 97025 are the relative amounts of elemental mercury and oxidized mercury. The ratio of elemental to oxidized mercury was reduced from 0.704 for coal 99626 to 0.153 for coal 97025. Comparing the blend fuel to its base fuel (coal 97025) an increase in chlorine content causes the elemental-to-oxidized ratio to drop to 0.011. Almost all mercury (98.9% of the total gaseous mercury) in the flue gas derived from the coal 97025 blend fuel exists in the oxidized form. In summary, the chlorine content of the fuel has an obvious influence on mercury emissions. Higher concentrations of mercury in the solid phase were obtained when the higher-chlorine-content coals were burned, since more elemental mercury was converted to oxidized mercury when higher-chlorine-content fuels were used.

The Effect of Limestone. To further evaluate the influence of chlorine content on mercury emission, two coals with close chlorine (~0.41%) and different sulfur contents (coal 98111 = 1.68% and coal 99626 = 4.48%) were also burned in this study. During both tests, the same Ca/S molar ratio (3.0) was used to control \( \text{SO}_2 \) emission in the flue gas. As a consequence, the limestone feeding rate used for burning coal 99626 was 1.67 times that used in the coal 98111 test. Mercury data shown in Figure 6 indicate that the percentage of gaseous mercury in the total fuel mercury was reduced from 37% (coal 98111) to 26.6% (coal 99626) as a result of the additional limestone. With regard to the different mercury species, oxidized mercury was reduced from
31% to 25.7% of total fuel mercury, while the elemental mercury was reduced from 6% to 0.9% of total fuel mercury. Apparently, the addition of more limestone can enhance mercury absorption on particulates. The identification of CaO as a dominant ash component and similarities in mercury–chlorine–CaO and mercury–chlorine–fly ash interactions also supports the assumption of CaO being an important mercury sorption component. In summary, the addition of limestone can help reduce mercury emissions as a catalyst for reactions of mercury and chlorine and as a sorbent for oxidized mercury.

Mercury Content in Fly Ash. Investigations at both the bench and laboratory scale with simulated flue gas have indicated some bituminous coal fly ashes and vapor-phase constituents play a role in the oxidation of elemental mercury. PRB/subbituminous coal fly ashes show higher adsorption capacities than bituminous coal fly ashes, but show, in most cases, very little mercury oxidizing capacity. Generally, the adsorption rate increases as the temperature in the flue gas decreases.

In addition to aiding in adsorption, laboratory- and pilot-scale studies have shown that solids such as activated carbon and fly ash can act as catalysts for the oxidation of elemental mercury. A study involving a series of bench scale experiments reported the catalytic effect of solids including traditional metal catalysts, activated carbon, and coal fly ash on the oxidation of elemental mercury in simulated flue gas in a fixed bed reactor. A study of fly ash from five different coals showed that coal fly ash converted gaseous elemental mercury to a mixture of gaseous oxidized mercury and adsorbed mercury at temperatures ranging from 150 to 360 °C. To date, the pilot-scale tests have shown the carbon-based catalyst to be the most effective in converting elemental mercury to Hg₂⁺.

A study of the effect of chlorine compounds on mercury sorption by fly ash indicated that the formation of a chloride solid phase did inhibit mercury sorption by fly ash. CaO with other Ca-based compounds inhibit the interaction of CaO with mercury. Interactions, which suggests that CaO is an important flue gas mercury sorption component and that chloride compounds inhibit the interaction of CaO with mercury. Figure 7 shows the mercury content in the fly ashes from firing four coals. The corresponding sulfur, chlorine, and carbon contents in fly ashes from five runs are shown in Table 4. The results indicate that fly ash is a better sorbent to capture mercury when it passes through FBC’s freeboard under relative low temperature (around 600 °C), especially for fly ash produced from high-chlorine coal. The fly ash from coal 99626 has the highest chlorine concentration among the four ashes and, as a consequence, the highest mercury content. The
The lowest mercury content was detected in the fly ash obtained from coal 99426.

The Effect of Secondary Air. Because of the different temperatures needed for capturing SO₂, HCl, and N₂O, as well as the oxidation of elemental mercury, two sets of secondary air nozzles were used, which inject air tangentially at an angle of 30° into the freeboard to form a strong vortex flow above the nozzles were used. The formation of a strong vortex above the nozzles increases the residence time of fine particles in the freeboard area allowing them to absorb more HCl by this swirling flow. The first layer of secondary air directly over the fluidized bed, which is operated at 850 °C, has a temperature of 950 °C to promote the combustion and desulfurization efficiency and to reduce N₂O and NOₓ emissions. The second layer of secondary air was operated at a temperature near 600 °C to provide high dechlorination efficiency to reduce the concentration of chloride species in the flue gas. The effect of secondary air on mercury emissions is shown in Figure 6. During this series of tests, the total air flow, bed temperature, coal feeding rate, and limestone feeding rate were held constant. Figure 8 clearly indicates that mercury emissions decrease significantly with an increase in the secondary/primary air ratio, resulting in a 70% reduction for coal 99626, 53% reduction for coal 98111, and 40% reduction for coal 97025. The effect of secondary air on the reduction of gas-phase mercury also increases with an increase in the chlorine content in the coal or in the addition amount of limestone (same chlorine content and different sulfur content), from 40% for coal 97025 (Cl = 0.21% and S = 3.06%), to 53% for coal 98111 (Cl = 0.41% and S = 1.67%), and followed by 70% for coal 99626 (Cl = 0.41% and S = 4.48%).

Conclusions

1. During the coal pyrolysis process, mercury in the coal was released in two stages. The first step is the emission of free mercury compounds in a drying process with the temperature being less than 350 °C. The second step is the emission of mercury associated with the organic matter in coal during the devolatilization process. Sixty percent of the total mercury in the coal was released in the second process.

2. Limestone addition only affects mercury release performance during coal pyrolysis. However, the addition of limestone can help reduce mercury emissions by acting as a sorbent or catalyst for oxidized mercury during the postcombustion process.

3. When a high-chlorine coal was burned, nearly 55% of the total fuel mercury was found in the solid phase (bed and fly ash). Of the mercury found in the solid phase, almost none was found in the bed ash because of its high surrounding temperature (850 °C). The gas-phase mercury, around 45% of total mercury input, was determined to be largely in the oxidized state (40% of the total mercury input), while only a small portion (4.5% of total mercury input) still existed as elemental mercury in the flue gas even when a high-chlorine (0.42 wt %) coal was burned without the benefit of a secondary air injection.

4. Fly ash is a better sorbent for capturing mercury when it passes through the FBC's freeboard at relatively low temperatures (around 600 °C), especially for fly ash produced from high-chlorine coal. Coal 99626 has the highest chlorine concentration among the four coals used and, as a consequence, its fly ash had the highest mercury content. The lowest mercury content was detected in the fly ash obtained from coal 99426, which had the lowest chlorine content.

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