Mercury emissions from selected stationary combustion sources in Korea

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Abstract

Mercury emissions from various stationary combustion sources such as coal-fired power plants, oil-fired power plants, industrial utility oil boilers, iron manufacturing plants, and industrial waste incinerators, were measured. The US EPA (Environmental protection agency) method 101A and the Ontario hydro method were used to sample the mercury containing combustion flue gases, at the inlet of the air pollution control devices (APCDs) and at the stack. Collected samples of both gaseous and particulate forms were then analyzed using CV AA (cold vapor atomic absorption) type analyzer. Measurement results from the coal-fired power plant showed percentages of elemental mercury (Hg\textsuperscript{0}) as high as 31.4\% and as low as 9.5\%. However, the content of Hg\textsuperscript{0} was in the range of 1.3–3.7\% from the industrial waste incinerator. Differences in mercury speciation from various stationary combustion sources are believed to be coming from: (1) difference in the fuel types; (2) difference in the major flue gas compositions (ex. HCl and SO\textsubscript{2}); and (3) difference in the types of air pollution control devices (APCDs). When the measurement results obtained using different sampling methods were compared, the Ontario Hydro Method gave a slightly higher mercury concentration measurement than that of the US EPA Method 101A.

Keywords: Mercury emission; Combustion sources; Mercury speciation; Ontario hydro method

1. Introduction

For the past few years, mercury has been a focus of extensive research by many toxicologists and environmental experts due to its high toxicity and a tendency to bio-accumulate, which are very threatening to both human and the ecosystem. According to the US EPA report (US EPA 1997a; US EPA, 1997b), major sources of mercury are combustion facilities such as coal-fired power plants, municipal solid waste incinerators (MSWIs), hazardous waste incinerators (HWIs), and medical waste incinerators, which, all together, account for approximately 87\% of total annual mercury emissions in the US alone.
In recent years, many countries began to implement the mercury emission standards for MSWIs and HWIs. For example, Germany has an emission standard for mercury of approximately 30 \( \mu g/m^3 \) (based on 11% \( O_2 \)) from incineration plants. In the US, HWI has to comply with new mercury emission limits based on maximum achievable control technology (MACT) standard, which is 45 \( \mu g/m^3 \) (based on 7% \( O_2 \)). Korea has a significantly lesser strict regulation of 100 \( \mu g/m^3 \) (based on 12% \( O_2 \)), which is to be implemented by year 2005.

In order to design a most effective mercury control technology for a given stationary source, it is critical to know the composition of the combustion flue gas. Extensive research has been carried out to develop an effective Hg sampling method for combustion flues gases. At present, the most widely-used sampling methods for Hg are the US EPA method 101A, the US EPA method 29, and the Ontario hydro method, which has been most-recently developed extensively for speciation of mercury (Hg\(^0\) and Hg(II)). Laudal et al. (1997) tested five different Hg sampling methods and found that the US EPA method 29 was not able to specify mercury properly for the coal-combustion flue gas. Using both the US EPA method 29 and the Ontario hydro method, Chang et al. (2000) evaluated Hg removal efficiency and speciation at two MSWIs with different flue gas compositions. They showed that Hg (II) was predominant in the flue gas from two MSWIs tested and the speciation came out differently depending on the types of APCDs. Hedrick et al. (2001) studied iodine based impinger solution for Hg\(^0\) using an inductively coupled plasma mass spectrometry (ICP-MS) with direct injection nebulization (DIN). Their results showed that Hg\(^0\) capture efficiency of the iodine-based solution was comparable to acidified potassium permanganate solution, and that over 98% of Hg\(^0\) was captured in the first oxidizing impinger solution.

In Korea, mercury related study and research suffers from the lack of emission database. The Korean Ministry of Environment is in the process of modifying the existing Korean standard method for mercury speciation in the combustion flue gas. In this study, for the first time, mercury emission from various types of stationary combustion sources in Korea were investigated using the US EPA method 101A and the Ontario hydro method for the purpose of (1) constructing a data base for mercury emission factor from various combustion sources in Korea and (2) developing a new Korean standard method for stack gas mercury speciation.

According to the type of fuel, operation capacity, and type of furnace, a total of 12 combustion facilities were selected (Table 1); coal-fired power plants, oil-fired power plants, iron manufacturing plant, and the industrial waste incinerators.
Throughout this study, the US EPA method 101A was used to sample the flue gas for Hg. The Ontario hydro method was tested at two stationary sources (coal-fired power plant and the industrial waste incinerator) to compare with the US EPA Method 101A and also for the speciation of mercury.

2. Experimental

Sampling of mercury in the flue gas was performed at the inlet of the APCDs and at the stack of all the stationary sources tested in this work using the US EPA method 101A. The Ontario hydro method was employed at two selected point sources; stacks of the coal-fired power plant and the industrial waste incinerator.

The US EPA method 101A uses only one type of acidified absorption solution (4 wt.% KMnO₄–10% H₂SO₄, first three impingers). The last impinger is packed with silica gel to collect moisture from the sampling gas. The Ontario hydro method is a modification of the US EPA method 29, employing an eight-impinger train and using three different absorption solutions; 1 N KCl (first three impingers), 5% HNO₃–10% H₂O₂ (fourth impinger), 4 wt.% KMnO₄–10% H₂SO₄ (next three impingers), and silica gel (last impinger). Unlike the US EPA method 101A, the Ontario hydro method is able to classify Hg⁰ and Hg (II), minimizing the possible interference by SO₂ of the flue gas in CVAA measurement. A specially designed stack gas sampler (Fig. 1) with a quartz-tipped stainless steel probe was used to insure the iso-kinetic sampling. Sampling was performed at least three times at each sampling point. As specified in both the US EPA method 101A and the Ontario hydro method, the US EPA methods 7470A and the US EPA method 7471A were used to prepare the gaseous and particulate samples for further analysis using a CVAA type Hg analyzer (M-6000A, Cetec).

3. Results and discussion

3.1. Concentration measurement and speciation

The results of mercury emission measurements from selected combustion sources, total of 12
facilities, are shown in Table 2. At the stacks of the Industrial oil-fired boilers (#1 and #2), total mercury emission concentrations ranged from 0.08 to 0.25 \( \mu g/m^3 \). Concentrations of total mercury measured at Oil-fired power plant were found to be 0.24–1.45 \( \mu g/m^3 \) at the inlet of the electrostatic precipitator (ESP) and 0.20–0.21 \( \mu g/m^3 \) at the stack. The lowest concentration for the total mercury emitted in this work agreed well with the value reported previously by the US EPA (US EPA, 1997a, 1998). Oil consuming combustor gave the lowest mercury concentration while the industrial waste incinerator gave the highest value.

For the coal-fired power plants tested, the types of coal and APCDs were the major factors affecting the level of total mercury emission concentration before and after the APCDs, respectively. The anthracite coal-burning facilities emitted higher concentration of total mercury than that of the bituminous coal-fired boilers. At Coal-fired power plant #1 burning domestic anthracite coal, mercury concentration was measured to be 10.44–37.77 \( \mu g/m^3 \) at the inlet of the ESP and 3.93–31.99 \( \mu g/m^3 \) out of the stack. Mercury emission concentrations measured at bituminous coal burning boilers (Coal-fired power plants #2 and #3) ranged between 1.01 and 5.41 \( \mu g/m^3 \) at the inlet of the APCDs (ESP + FGD) and between 2.03 and 4.39 \( \mu g/m^3 \) at the stack. Emission concentrations of Hg both at the inlet of the APCDs and out of the stack were very sensitive to the following factors: coal characteristics, APCDs’ momentary condition, the variation of incoming mercury amounts, and flue gas temperature (Laudal et al., 2000; Miller et al., 2000). In addition, fly ash may continuously adsorb and desorb Hg from and back

Table 2 Results of mercury emission measurements from selected combustion sources

<table>
<thead>
<tr>
<th>Combustion source</th>
<th>Emission conc. (( \mu g/Sm^3 ))</th>
<th>Type of APCDs</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Inlet of the APCDs</td>
<td>At the stack</td>
<td></td>
</tr>
<tr>
<td>Industrial oil-fired boiler #1</td>
<td>N.A.</td>
<td>0.21–0.25</td>
<td>Multi cyclone</td>
</tr>
<tr>
<td>Industrial oil-fired boiler #2</td>
<td>N.A.</td>
<td>0.08–0.16</td>
<td>Multi cyclone</td>
</tr>
<tr>
<td>Oil-fired power plant</td>
<td>0.24–1.45</td>
<td>(Avg. 0.65)</td>
<td>ESP</td>
</tr>
<tr>
<td>Coal-fired power plant #1</td>
<td>10.44–37.77</td>
<td>(Avg. 23.45)</td>
<td>ESP + FGD</td>
</tr>
<tr>
<td>Coal-fired power plant #2</td>
<td>1.01–5.41</td>
<td>(Avg. 1.78)</td>
<td>ESP + FGD</td>
</tr>
<tr>
<td>Iron manufacturing plant #1</td>
<td>0.69–4.20</td>
<td>(Avg. 2.04)</td>
<td>Bag filter</td>
</tr>
<tr>
<td>Iron manufacturing plant #2</td>
<td>6.47–8.58</td>
<td>(Avg. 7.29)</td>
<td>Bag filter</td>
</tr>
<tr>
<td>Iron manufacturing plant #3</td>
<td>13.27–14.05</td>
<td>(Avg. 13.66)</td>
<td>ESP</td>
</tr>
<tr>
<td>Industrial waste incinerator #1</td>
<td>619.23–1318.14</td>
<td>(Avg. 968.68)</td>
<td>Cooling chamber + Cyclone + Spray tower + Wet ESP</td>
</tr>
<tr>
<td>Industrial waste incinerator #2</td>
<td>56.27–59.26</td>
<td>(Avg. 57.77)</td>
<td>Dry scrubber</td>
</tr>
<tr>
<td>Industrial waste incinerator #3</td>
<td>14.27–34.77</td>
<td>(Avg. 23.51)</td>
<td>Semidry scrubber</td>
</tr>
</tbody>
</table>
into the flue gas depending on the momentary flue gas temperature (Sjostrom et al., 2001). There are two major types of furnace used for iron manufacturing plants; electric and sintering. In the case of an electric furnace, the Hg concentrations ranged from 0.69 to 8.59 µg/m³ at the inlet of the filter bag and from 0.75 to 1.04 µg/m³ out of the stack. For the sintering-furnace iron manufacturing plant, 13.27–14.05 µg/m³ of Hg was measured at the inlet of the ESP and 10.18–19.12 µg/m³ was measured at the stack. Temperatures at upstream and downstream of APCDs were in the range of 153–180 °C and 172–180 °C, respectively, for the sintering-furnace iron manufacturing plant. The variation in Hg emissions from iron manufacturing plants was due to the intermittent operating condition of melting processes.

The highest Hg emission value was recorded at the industrial waste incinerator due to the high mercury contents in industrial hazardous wastes and the ranges of Hg concentration were quite broad. Fluctuation of the industrial waste characteristics (non-homogeneity) fed into the furnace resulted in the fluctuation in effluent Hg concentration. For Industrial waste incinerator #1, the mercury emission ranged 619.23–1318.14 µg/m³ at the inlet of wet type particulate control device and 40.72–325.65 µg/m³ at the stack. Industrial waste incinerators #2 and #3 with dry- and semidry-type APCDs (scrubber+bag filter) emitted mercury in the range of 14.27–59.26 µg/m³ at the inlet of APCDs and 17.80–58.76 µg/m³ at the stack. A Hg removal efficiency was calculated based on the ratio of concentrations at the inlet of APCDs and at the stack. The results show that industrial waste incinerator with a wet-type APCDs (Industrial waste incinerator #1) have achieved 85.6% Hg removal efficiency while incinerators with dry- or semidry-type APCDs (Industrial waste incinerators #2 and #3) have achieved only 21.1% and 9.6%, respectively. These results indicate that oxidized form of Hg (by strong oxidizer such as HCl and SOₓ) is predominant in the incinerator flue gas, which can be readily removed in the wet-type scrubber due to its high solubility in an acidic solution (Carpi, 1997; Krivanek, 1996; Laudal et al., 2000; Miller et al., 2000).

### 3.2. Comparison of the US EPA method 101A and the Ontario hydro method

Mercury sampling was performed simultaneously using the US EPA method 101A and the Ontario hydro method at two sampling points; stacks of the Coal-fired power plant #3 and Industrial waste incinerator #2. Table 3 shows the measured concentrations of mercury as well as the fractions of Hg⁰ and Hg(II) in the flue gas. Concentrations of two major chemical constituents in the combustion flue gases, which were believed to have significant effect on the mercury speciation -HCl and SOₓ-
were also measured at the stack; 1) 8.6 ppm-HCl and 32.8 ppm-SO$_2$ (Coal-fired power plant #3) and 40.6 ppm-HCl and 68.5 ppm-SO$_2$ (Industrial waste incinerator #2). HCl was sampled using Korean standard method and analyzed by the ion chromatography (model DX-120, Dionex), whereas, SO$_2$ was analyzed directly by the Stack gas analyzer (Kane-May 9106, UK).

At the Coal-fired power plant #3, mercury concentration ranged from 2.20 to 2.26 µg/m$^3$ when sampled by the US EPA method 101A and from 2.11 to 2.41 µg/m$^3$ when sampled by the Ontario hydro method. At the Industrial waste incinerator #2, mercury emission concentration ranged 23.70–58.76 µg/m$^3$ for the US EPA method 101A and 42.17–72.21 µg/m$^3$ for the Ontario hydro method. In this work, average values from the samples obtained by the Ontario hydro method sampling were slightly higher than those by the US EPA Method 101A (Table 3).

Meanwhile, the average distributions of both Hg$^0$ and Hg (II) in the flue gases were obtained using the Ontario hydro method. Elemental mercury in the coal combustion flue gas (Coal-fired power plant #3) ranged from 84.4 to 85.5% and oxidized mercury ranged from 14.5 to 15.6% (Table 3). However, Hg$^0$ ranged 1.3–3.7% and Hg(II) ranged 96.3–98.7% in the flue gas from Industrial waste incinerator #2 (Table 3). This results can be expected since combustion sources such as hazardous waste incinerator, municipal solid waste incinerator, and medical waste incinerator exhibit relatively high contents of acidic gases (HCl, SO$_2$, Cl$_2$, etc.), which are capable of oxidizing Hg$^0$ to Hg(II). In other words, a greater fraction of Hg$^0$ is found for the coal combustion flue gases than those of waste incinerators suggesting that an extra effort should be implemented for coal combustion since the Hg$^0$ is more difficult to deal with due to its pure solubility and high volatility. However, emission characteristics of Hg from combustion sources are very source-dependent and source-specific. Therefore, a customized and an extensive research on a specific stationary source must precede to design most effective method for Hg emission control.

4. Conclusions

To investigate the Hg emission characteristics from stationary combustion sources in Korea, Hg sampling was carried out at 12 selected combustion facilities. It was found that the Hg emission was dependent on fuel type, APCDs configuration, and flue gas condition. The lowest Hg concentration was obtained from an oil consuming combustor while the highest value was recorded at the industrial incinerator. Type of coal was a major factor characterizing the Hg emission from coal-fired utility boilers; anthracite coal with a higher concentration of Hg emitted than bituminous coal. Understanding that the emission characteristics are very source-dependent and source-specific, flue gas speciation results in this study showed that larger portion of Hg$^0$ was found in coal-fired utility boilers while Hg (II) was dominant at industrial waste incinerators.

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