Research on the Status of Mercury Pollution Prevention in the Flue Gas of Coal-fired Power Plants

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Abstract. This paper introduces the current situation of mercury pollution from coal burning, the forms and characteristics of mercury emission and mercury emission standards at home and abroad. The advantages and disadvantages of different mercury monitoring methods and detection techniques were analyzed. 32 units of 16 power plants selected as the pilot in China, analyzed the current situation of mercury emission from coal-fired power plants and the influencing factors of mercury emission concentration through manual monitoring and automatic monitoring, and proposed the research direction of mercury emission control technology in the future.

Introduction

Mercury is persistent, migrate easily, bioaccumulative and highly toxic, and it is harmful to human health and ecological environment. Improper use or discharge can cause serious environmental pollution and endanger human health and ecological security. It has become a pollutant that needs control strictly after dust, SO2 and NOx in coal-fired power plants. Burning coal accounts for about 40 percent of global mercury emissions. China accounts for about 60% of the world's coal consumption and has become one of the most polluted areas of mercury in the world. Emission standard of air pollutants for thermal power plants included mercury and its compound concentration in emission limits for the first time, marking that the control of atmospheric mercury pollution in China has been formally put on the agenda. China formally signed the international mercury control convention in 2013[1]. Therefore, China is facing great pressure of mercury emission reduction from the perspective of international implementation and domestic mercury pollution prevention.

Mercury emission standards for domestic and foreign coal-fired power plants

The United States. On December 16, 2011, the United States environmental protection agency (EPA) issued the first mercury and air toxics standards (MATS) for coal-fired power plants, including limits on toxic and hazardous gaseous pollutants from coal-fired fuel units and boiler performance specifications for new fossil fuel units. The new mercury emission limits for new units built and existing units after May 3, 2011 have been implemented since April 16, 2015, as shown in the table below\textsuperscript{[2-4]}.
continental (excluding limited-use liquid oil-fired subcategory units) | | | |
<table>
<thead>
<tr>
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</tr>
</thead>
<tbody>
<tr>
<td>Liquid oil-fired unit - non-continental (excluding limited-use liquid oil-fired subcategory units)</td>
<td>0.0004</td>
<td>0.05</td>
<td>0.0004</td>
</tr>
<tr>
<td>Solid oil-derived fuel-fired unit</td>
<td>0.002</td>
<td>0.27</td>
<td>0.002</td>
</tr>
</tbody>
</table>

40 CFR Part 63, Subpart UUUUU (2018 update) stipulates that the mercury emission limit of a new unit of non-low rank coal is 0.003lb/(GW•h). Other units have the same mercury emission limit as MATS.

**European Union.** The European Union has not set a limit on mercury emissions on the limitation of emissions of certain pollutants into the air from large combustion plants and Best Available Techniques for Large Combustion Plants, Germany's GFAVO amended in 2004, sets limits on mercury emissions from coal-fired power plants by limiting mercury and its compounds to no more than 30μg/m³.

**China.** GB13223-2011 issued on July 29, 2011, refers to the emission limit of GFAVO, which stipulates that the emission limit of mercury and its compounds executed is 30μg/m³ by Chinese coal-fired boilers starting from January 1, 2015.[5]

**Compared** with mercury emission limit value of MATS, our mercury emission limit value is relatively loose. The most relaxed mercury emission limit in MATS is for existing and newly built units that burn low-grade coal, both of which are 5.4μg/m³. But it’s still below the mercury emission limit value of our country.

**Distribution of mercury in flue gas**

Mercury is affected by many factors such as boiler configuration, boiler operation state, coal type, combustion atmosphere, flue gas velocity and cooling rate, air pollution control device, etc. in coal combustion process. Generally, the mercury content in the bottom ash is less than 2%, and most of the mercury is released into the flue gas in the elemental form. After the coal powder is burned in the boiler, all the mercury produced is the elemental mercury. As the temperature decreases (750 ~ 900K), the elemental mercury will undergo a series of homogeneous oxidation reactions, and part of Hg⁰(g) will be oxidized to Hg²⁺(g) in the gas phase. The remaining elemental mercury will be catalyzed by fly ash particles to become bivalent mercury at a lower temperature (400-600k) and adsorbed on grey particles, mainly forming particulate mercury Hg⁰ from Hg⁰(g) and Hg²⁺(g).

Therefore, Hg mainly exists in three forms, namely Hg⁰, Hg²⁺ and Hg⁰. The proportion of mercury in the flue gas of different coal is different. Hg⁰ accounts for 20% (mass fraction, the same below) of total mercury in the flue gas of bituminous coal after combustion, Hg²⁺ accounts for 35%, and Hg⁰ accounts for the highest proportion, 45%. Hg⁰ accounts for 65% of the total mercury, Hg²⁺ and Hg⁰ account for 20% and 15% respectively. The content of Hg⁰ in the flue gas after lignite combustion is the highest, accounting for 85% of total mercury, Hg²⁺ and Hg⁰ is very small, accounting for 10% and 5%, respectively.

Hg²⁺ is soluble in water and can be removed by wet method (such as wet desulfurization system of coal power plant). Hg⁰ can be removed with fly ash in the dust removal equipment; However, Hg⁰ makes use of existing pollutant control equipment of coal-fired boilers, which is difficult to remove, and almost all of them are released into the atmosphere. It stays for a long time and is easy to migrate, thus causing global pollution. The configuration and characteristics of coal mercury emission are shown in the following table[6].
Table 2 Morphology and characteristics of mercury emission from coal burning

<table>
<thead>
<tr>
<th>Morphology</th>
<th>character</th>
<th>Collection method and effect</th>
<th>Influence factors</th>
</tr>
</thead>
<tbody>
<tr>
<td>influence factor</td>
<td>Highly volatile, insoluble in water, long in the atmosphere, can be adsorbed under certain conditions</td>
<td>Difficult to be collected by dust remover and removed by wet desulfurization</td>
<td>Temperature and flyash characteristics</td>
</tr>
<tr>
<td>Oxidation state mercury</td>
<td>Water-soluble, volatile and easy to be adsorbed</td>
<td>Be partially adsorbed on the surface of particulate matter and collected by dust collector</td>
<td>Temperature, fly ash characteristics, halogen content of flue gas</td>
</tr>
<tr>
<td>Particulate mercury</td>
<td>Adsorbed on the surface of fly ash or carbon residue and charged in the electrostatic precipitator easily, has a short residence time in the atmosphere</td>
<td>Easy to be collected by dust collector</td>
<td>Temperature and flyash characteristics</td>
</tr>
</tbody>
</table>

**Monitoring methods of mercury emission from coal-fired flue gas**

At present, the mercury monitoring methods of coal-fired power plants mainly include Ontario Hydro Method, 30A method and 30B method.

The Ontario Hydro, which includes sample collection, recovery, digestion and analysis testing, is a standard method for mercury testing of flue gas commonly used in coal-fired power plants, with a measurement range of 0.5-100 μg/m³. It can be used for manual sampling and monitoring of different flue duct locations before SCR reactor, air preheater and dust collector, and can measure the respective concentration and total mercury concentration of three different forms of mercury in flue gas. The deficiency of this method is that the operation is more complex, which is greatly affected by human factors. Compared with 30A and 30B, the minimum detection limit is higher in Ontario Hydro Method.

The 30A method is to monitor the mercury emission using the on-line continuous monitoring system (Hg-CEMS). It is applicable to the determination of mercury emission concentrations at ground, chimney outlets and fixed flue locations with monitoring platforms. The measurement range is 0.02-200 μg/m³. Continuous mercury emission data can be obtained by the 30A method, and gaseous Hg⁰ and gaseous Hg²⁺ can be measured respectively. The disadvantages are complex and expensive equipment and high maintenance cost.

The 30B method, also known as the off-line sampling method of the adsorption tube, namely the absorption sampling first and then desorption for concentration analysis, can measure the concentration of total gaseous mercury in the flue gas, which does not support the mercury morphology monitoring. The measuring range is 0.1-50 μg/m³. Hg⁰ can not be collected by this method, and the analytical flue gas is required to be purified. Therefore, the sampling point is usually located after the flue gas purification device. Relatively speaking, the 30B method is simple and convenient to operate, with high measurement accuracy. It is widely used in the international manual measurement of total atmospheric mercury emissions from coal-fired power plants. Based on the 30B method, China is developing a mercury emission monitoring method suitable for domestic coal-fired power plants, selecting and developing corresponding monitoring equipment.

At present, the technology of mercury analysis and detection has been mature, mainly including cold steam atomic absorption spectra, cold steam atomic fluorescence spectra and zeeman modulation atomic fluorescence spectra and so on. All the testing technologies analyze for Hg⁰, and the comparison of them is shown in the following table.
<table>
<thead>
<tr>
<th>Technology</th>
<th>Advantage</th>
<th>Disadvantage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cold steam atomic absorption spectrum</td>
<td>Installed on site without external gas source support</td>
<td>Elemental mercury only</td>
</tr>
<tr>
<td>Cold steam atomic fluorescence spectra</td>
<td>With lower spectral interference and superior linear index, the sensitivity can reach 0.001 μg/m³</td>
<td>Elemental mercury only</td>
</tr>
<tr>
<td>Zeeman modulates the atomic fluorescence spectrum</td>
<td>Little interference and no pre - enrichment and desorption process</td>
<td>Dual channel design required</td>
</tr>
</tbody>
</table>

**Mercury emission from coal-fired units in China**

Late 2011 and early 2012, Ministry of environmental protection had issued the monitoring program for pilot monitoring of atmospheric mercury emissions from coal-fired power plants and the notice on continuing pilot monitoring of atmospheric mercury emissions from coal-fired power plants. A total of 32 units of 16 coal-fired power plants distributed in 12 provinces or cities or autonomous regions, which reflects the basic situation of coal-fired power plant units in China to a large extent. The monitoring results are shown in the following table.

**Table 4 Statistical table of monitoring results**

<table>
<thead>
<tr>
<th>Monitoring method</th>
<th>Coal</th>
<th>Mean mercury concentration [μg·m⁻³]</th>
<th>Number of unit</th>
<th>Number of exceeding unit</th>
<th>Proportion [%]</th>
<th>Standard limit value [μg·m⁻³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Manual monitoring</td>
<td>Burning non-low rank coal</td>
<td>4.83</td>
<td>66</td>
<td>0</td>
<td>0</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>Burning low rank coal</td>
<td>3.97</td>
<td>50</td>
<td>36</td>
<td>72</td>
<td>1.76</td>
</tr>
<tr>
<td>Automatic monitoring</td>
<td></td>
<td>7.52</td>
<td>16</td>
<td>8</td>
<td>50</td>
<td>5.4</td>
</tr>
</tbody>
</table>

By combining the manual monitoring and automatic monitoring data with the content of mercury and carbon in coal, it was found that the mercury emission concentration in flue gas was correlated with the content of mercury and carbon in coal. The mercury emission concentration of non-low-rank coal is lower than that of low-rank coal. The lower the mercury content in the coal, the higher the carbon content, the lower the mercury emission concentration.

The low-rank coal mainly includes lean coal, lignite, and non-low-rank coal mainly includes anthracite, bituminous coal and so on in China. The total mercury content of low rank coal is higher than that of non-low rank coal. The carbon content of non-low-rank coal is higher than that of low-rank coal, and the higher the carbon content of coal, the more fly ash will be generated after full combustion. After the dust removal and desulfurization equipment, the removal effect of mercury is more obvious. Therefore, when coal-fired power plants burn low-rank coal and non-low-rank coal, there is a difference in mercury concentration in the flue gas.

In the ultra-low emission reconstruction technology, SCR denitration technology is helpful for the removal of mercury in flue gas. The effect of ultra-low emission reconstruction technology, such as dust removal and desulfurization, on the removal rate of mercury in flue gas needs further study.

**Conclusions**

The mercury concentration in the external flue gas under manual monitoring and automatic monitoring is far lower than the GB13223-2011 emission limit, and all the units have achieved the standard emission.

Based on the mercury emission limits of non-low-rank and low-rank coal in the existing sets of MATS, 66.7% of the mercury emission in the manually monitored units exceeds the standard, and 77.4% of the mercury emission in the self-monitored units exceeds the standard.
Based on existing desulfurization, including denitrification and dedusting facilities of coal-fired power plants, the technology of coordinated control of mercury emission and its influencing factors should be further studied.

References


