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Mercury speciation and its emissions from a 220 MW pulverized coal-fired boiler power plant in flue gas

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Abstract–Distributions of mercury speciation of Hg^0, Hg^{2+} and Hg^P in flue gas and fly ash were sampled by using the Ontario Hydro Method in a 220 MW pulverized coal-fired boiler power plant in China. The mercury speciation was varied greatly when flue gas going through the electrostatic precipitator (ESP). The mercury adsorbed on fly ashes was found strongly dependent on unburnt carbon content in fly ash and slightly on the particle sizes, which implies that the physical and chemical features of some elemental substances enriched to fly ash surface also have a non-ignored effect on the mercury adsorption. The concentration of chlorine in coal, oxygen and NO_x in flue gas has a positive correlation with the formation of the oxidized mercury, but the sulfur in coal has a positive influence on the formation of elemental mercury.

Key words: Coal-fired Boiler, Mercury Speciation, Mercury Emission, Flue Gas, Fly Ash

INTRODUCTION

In coal-fired flue gas, the different speciation of mercury will cause direct or latent harm to human health. A global mercury mass balancing model showed that 34% of the atmospheric mercury originates from coal burning [1], which is also known as the biggest anthropogenic atmospheric mercury release source [2]. The US EPA submitted a report to Congress in 1997 that also pointed out 33% of anthropogenic mercury was coming from coal-fired power plants [3]. The distribution of mercury's speciation in coal-fired flue gas has tremendous influence on mercury's removal as well as the migration transformation [4]. There are at least three kinds of speciation of mercury: elemental mercury (Hg^0), gaseous oxidized mercury (Hg^{2+}) and particle-bound mercury (Hg^p) [5]. Different speciation of mercury has different physical and chemical properties. Gaseous oxidized mercury is easily dissolvable in water, and easily adsorbed by particles in flue gas, therefore easily separated by wet desulphurization devices, conventional dust removal equipment such as electrostatic precipitator (ESP) or fabric filter (FF). Particle-bound mercury is usually formed from oxidized mercury and also easily collected by dust removal advices. However, elemental mercury is not dissolvable in water; a dust collector or desulphurization equipment has great difficulty in trying to capture it. Therefore, it's very important to analyze the distribution of mercury's speciation in flue gas, especially the factors affecting mercury's speciation and its distribution for its removal.

In order to actively control mercury emissions, some countries started research on the distribution of mercury's speciation in recent years, trying to find an effective method for mercury removal. In 1994 Finkelman [6] studied the mechanism of raw coal with the harmful element release; Devito [7] compared the trace element emission caused by raw coals used in a power plant; Helble [8] conducted research on the micron harmful element distribution in the gasification process. In Korea, research on removal of mercury and other heavy metals has been done and valuable conclusions obtained [9-11]. In recent years, China started related research on trace elements on their characteristics and distribution in coal-fired flue gas [12]. This paper reports the mercury field measurement results based on the US EPA recommended Ontario Hydro Method (OHM), which was carried out in a Chinese 220 MW utility pulverized coal boiler system, and the mercury speciation and distribution characteristics were obtained in the power plant.

EXPERIMENTAL

The Ontario Hydro Method was used to sample the flue gas. Samples are withdrawn from the flue gas isokinetically through a probe/filter system, maintained at 120 °C or above the flue gas temperature, and flow through a series of impingers in which different chemical solutions are used to detect the mercury speciation that are immerged in an ice bath. Particle-bound mercury in the flue gas is collected in a filter at the front tip of the sampling probe. Oxidized mercury is collected in three impingers containing a chilled aqueous potassium chloride solution. Elemental mercury is collected in subsequent impingers (one impinger containing a chilled aqueous acidic solution of hydrogen peroxide and three impingers containing chilled aqueous acidic solutions of potassium permanganate). Samples are recovered, digested, and then detected in a Leeman Labs Hydra AA automated mercury analyzer based on the cold-vapor atomic absorption spectrum (CVAAS) principle.

Fig. 1 and Fig. 2 show, respectively, schematic diagrams of the

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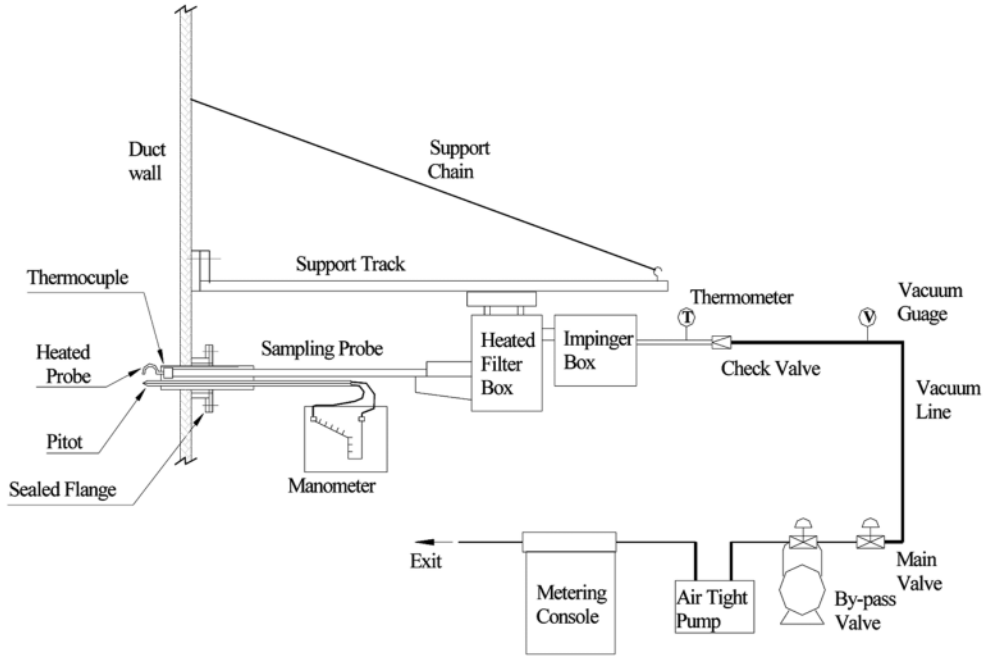

Fig. 1. Isokinetic sampling system of flue gas mercury by OHM method.

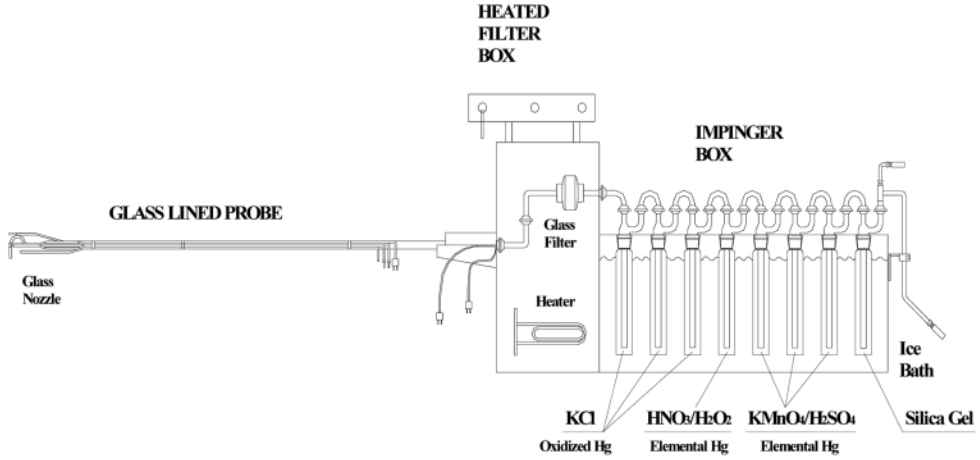

Fig. 2. The chemical solutions absorbing flue gas mercury speciation in OHM system.

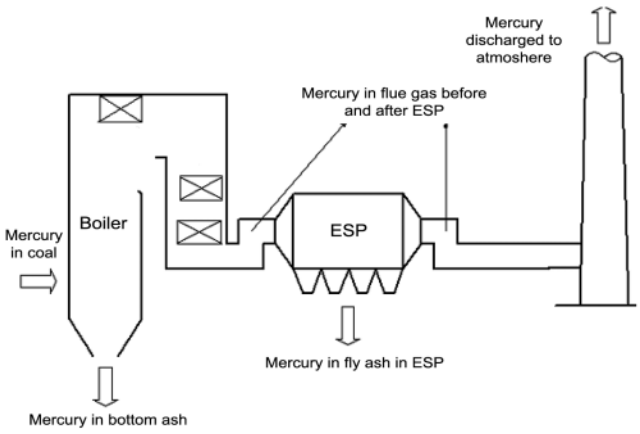

Fig. 3. Mercury sampling locations in the 220 MW PC boiler with ESP system.

isokinetic sampling system of flue gas mercury by Ontario Hydro Method and the chemical solutions absorbing flue gas mercury speciation in OHM system. A selected 220 MW power plant of pulverized coal-fired boiler system in China was used to conduct sampling of the mercury speciation before and after the ESP along with sampling in coal, bottom ash and fly ashes below the ESP, as shown in Fig. 3. In order to obtain the samples accurately, the coal samples are collected in the air-coal powder pneumatic conveying duct immediately before burners, the bottom ash is sampled on the belt of the slag discharging machine, the flue gas samples use the OHM sampling system before and after ESP, respectively, at the same time, and the fly ashes in the four ESP electric fields are drawn by a vacuum pump. The mercury speciation and distribution characteristics of this 220 MW power plant were obtained.

RESULTS AND DISCUSSIONS

Table 1. Averaged ultimate and approximate analyses and trace element contents in coal

C %	H %	N %	S %	O %	W %	A %	V %	FC %	Hg mg/kg	Cl mg/kg	HHV MJ/kg
68.86	4.67	1.38	0.38	8.12	9.18	7.42	27.81	55.6	0.009955	267	27.036

Table 2. Averaged unburnt carbon (UC), ash and Hg contents in bottom and ESP ashes

Items	Units	Bottom ash	ESP ash
UC	%	0	2.36
Ash	%	100	97.64
Hg	mg/kg	0.001255	0.007055

Table 3. Averaged mercury speciations contents in flue gas before and after ESP

Items	Units	Before ESP	After ESP
Hg^0	μg/Nm^3	1.6155	1.0194
Hg^{2+}	μg/Nm^3	0.0884	0.0821
Hg^p	μg/Nm^3	0.0079	3.49E-06

1. Mercury Speciation and Distribution in Flue Gas

The measured total mercury concentrations in flue gas in five separate cases under full load of boiler operation conditions were found to be less than 2 μg/Nm^3 since the coal used is Shenhua bituminous coal with very little mercury content only averaging 0.01 mg/kg, which is in accordance with the literature [13,14]. Table 1 lists the averaged ultimate and approximate analyses and trace element contents in coals. Table 2 shows the averaged unburnt carbon, ash and mercury contents in bottom and ESP electric field ashes, and Table 3, the averaged mercury speciation concentrations measured in the flue gas before and after ESP.

The results of mercury speciation from Table 3 show that the total vapor phase mercury (Hg^{2+} and Hg^0) in flue gas after the ESP occupies a quite big proportion up to 92% compared with the data from US EPA's Information Collection Request (ICR) [15] that indicates a total vapor phase mercury in flue gas after ESP averages 60%. The above results verify that the mercury removal efficiency through the ESP is so low in this case because the oxidized mercury and the particulate mercury in flue gas are very little both before and after the ESP. Of the total mercury in flue gas, the proportion of Hg^{2+} is about 5.16% before ESP and 7.44% after ESP, while that of the Hg^0 is about 94.38% before ESP and 92.53% after ESP, as well as that of the Hg^p is only 0.46% before ESP and 0.03% after ESP. The reason is that chlorine in coal is much lower (140-170 mg/kg) at most of the test conditions. Because of high combustion efficiency of the boiler, the unburnt carbon in fly ash is extremely low at a mean of 2.36%, which leads to the very low oxidized mercury as well as the particle-bound mercury.

Of some factors affecting the flue gas oxidized mercury, chlorine in coal is as active as the flue gas temperature. Because of the instantaneous content of chlorine and mercury in coal feeding into the boiler is changing, the flue gas mercury speciation concentration is changing also. Fig. 4 shows the ratio of oxidized mercury to total mercury in flue gas affected by chlorine contents in five feeding coals. The chlorine content is very close for the four kinds of

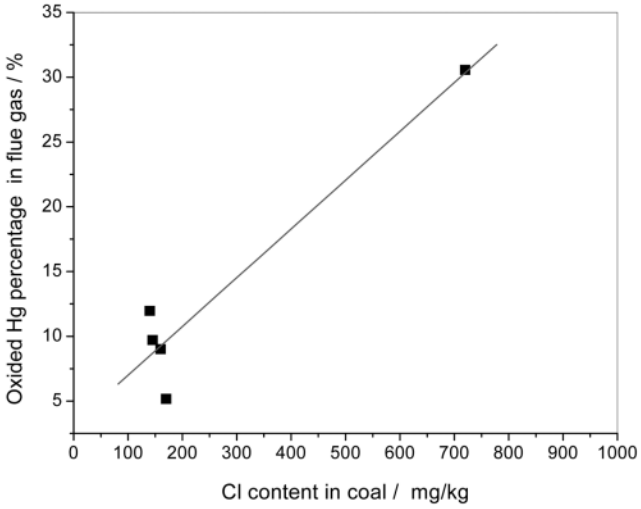

Fig. 4. Oxidized Hg percentage in flue gas vs. Cl content in coal.

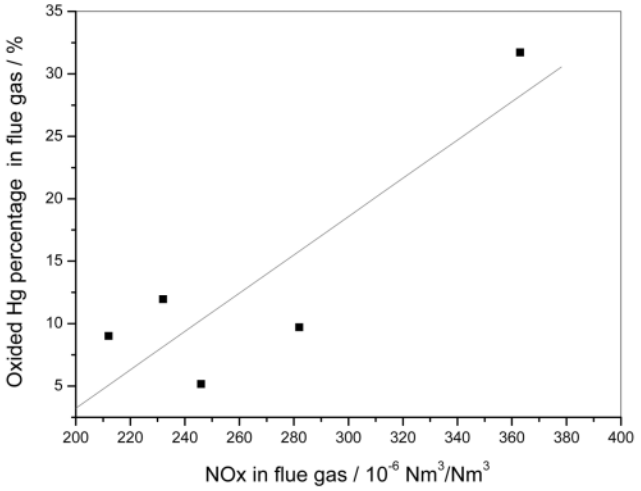

Fig. 5. Oxidized Hg percentage in flue gas vs. NO_x content in flue gas.

coals ranging from 140-170 mg/kg while the fifth coal sharply reaches 720 mg/kg as a result that the oxidized mercury percentage is also sharply increased. Generally speaking, with increasing of the coal chlorine content, the oxidized mercury percentage increases [16].

In flue gas, NO_x and oxygen also influence the mercury speciation and its distribution shown in Fig. 5 and Fig. 6. Having some catalytic effect and making the flue gas oxidized, NO_x and oxygen may cause partial elemental mercury to be oxidized. Thus, the higher the content of both, the higher the ratio of oxidized mercury.

The particle-bound mercury proportion is very small in flue gas, is only 0.46% before ESP and 0.03% after ESP. It is found that the particle-bound mercury is correlated closely to the fly ash particles' physical and chemical properties. The fly ash size distribution and unburned carbon content needs to be paid double attention. The lat-

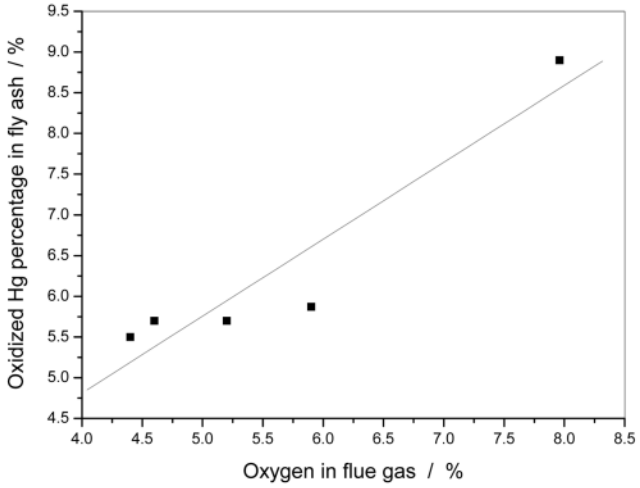

Fig. 6. Particulate bound Hg percentage vs. O_2 content in flue gas.

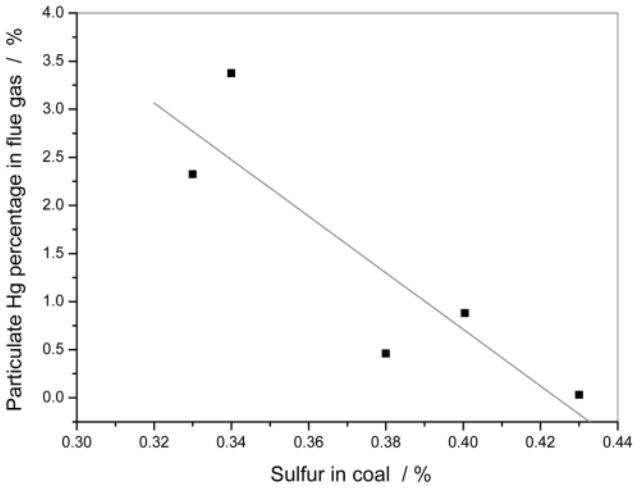

Fig. 8. Particle-bound Hg percentage vs. S content in coal.

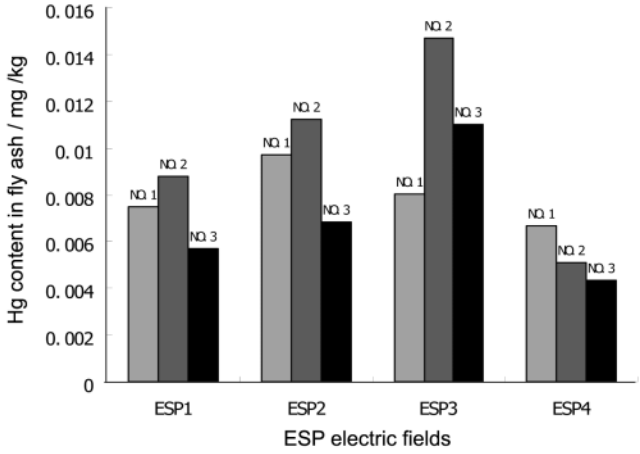

Fig. 7. Hg content in fly ash under three cases of full boiler load vs. ashes from ESP electric fields.

ter clearly displays strong positive correlation to the mercury adsorption [17]. From the viewpoint of effective control of mercury, the activated carbon may be the most effective mercury adsorbent.

In this test, the mercury content of fly ash samples was analyzed in three cases of full load boiler operation conditions that were denoted as No. 1, No. 2 and No. 3 and sampled from each of the four ESP electric fields denoted as ESP1, ESP2, ESP3 and ESP4 shown in Fig. 7. It can be seen that from first to fourth electric field, fly ash particle size gradually reduces, but its mercury content firstly gradually increases until to the second or third electric field and then reduces in the fourth. Three cases of samples showed the same trend. It is assumed that when the fly ash surface adsorbs other trace elements such as arsenic, selenium and so on, those various elements have different physical and chemical properties; they will make strong effects for fly ash to adsorb the mercury [18]. Obviously, the mechanism of fly ash adsorption for mercury should be further studied.

Some researchers have indicated that the particle-bound mercury adsorbed on fly ash is mainly $HgSO_4$(s) and HgO(s); therefore, the oxygen content in flue gas and the sulfur content in coal are recognized as some influences on the particle-bound mercury, demonstrated in Fig. 6 and Fig. 8 for five runs of coals feeding into the boiler under condition of full load boiler operations. With increasing of the oxygen content in flue gas, the particle-bound mercury in fly ash increases also. However, with increasing of the sulfur content in coal, the particle-bound mercury decreases. The reason is that when the oxygen content increases, the atmosphere for both flue gas and fly ash trends to form oxidation that makes the oxidized mercury formed easily. But the sulfur can cause the mercury oxidization temperature range to be narrowed, which makes the elemental mercury increased [19] and oxidized mercury decreased.

CONCLUSIONS

1. The flue gas mercury speciation and its distribution in a selected 220 MW pulverized coal boiler system showed that, owing to very low Cl content of averaged 267 mg/kg in coals, the oxidized mercury in flue gas is very small compared with the very high elemental mercury.

2. The chlorine content in coal has a positive correlation on formation of oxidized mercury. Whereas, the sulfur content in coal has a positive correlation to formation of elemental mercury.

3. The flue gas component has an important influence on the mercury speciation. With increasing of the oxygen and NO_x content in flue gas, the particle-bound mercury proportion increases. However, with increasing of the sulfur content, the particle-bound mercury proportion decreases.

4. It is found that the particle-bound mercury is correlated closely to the physical and chemical properties of the fly ash particles. The fly ash size distribution and unburned carbon content needs double attention. The latter clearly displays strong positive correlation to the mercury adsorption.

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