

Multi-method mercury specification from lignite-fired power plants

Ping Lu^{*,†}, Jiang Wu^{**}, and Wei-ping Pan^{***}

^{*}School of Power Engineering, Nanjing Normal University, Nanjing 210042, China

^{**}School of Energy & Environmental Engineering, Shanghai University of Electric Power, Shanghai 200090, China

^{***}ICSET, Western Kentucky University, Bowling Green, KY 42101, USA

(Received 17 July 2008 • accepted 15 October 2008)

Abstract—Mercury concentration and speciation partitioning, including total mercury, elemental mercury and oxidized mercury from a lignite-fired power plant under different operating conditions, was studied by Ontario hydro method (OHM), two kinds of continuous mercury monitors (semi-continuous emission monitor (SCEM) and continuous mercury monitor (CMM)), and the sorbent trap method. The effects of boiler load, fuel blending ratio, electrostatic precipitator, flue gas desulphurization, flue gas bypassing the FGD ratio, and mercury measuring methods on mercury emission were analyzed. The results indicated that mercury data from OHM, SCEM and CMM presented a good consistency throughout the entire testing period within $\pm 20\%$ acceptable range; however, the results from Appendix K provided bigger discrepancies than the results of OHM and SCEM due to the interferences of higher selenium content in the flue gas. The particulate-bound mercury removal efficiencies of ESP were determined to be 16-35%. The percentages of elemental mercury emitted from two lignite-fired power plants were in the higher ranges of 43.9-74.2%.

Key words: Mercury Emission, Lignite-fired PC Boiler, Hg Measuring Method, Field Testing

INTRODUCTION

Mercury emission as a global air pollution problem is attracting more and more attention world-wide. Of all the anthropogenic mercury emissions, coal-fired electric utility boilers have been reported as the largest single category, contributing about one third of total anthropogenic mercury emissions [1-3]. The US EPA set the final regulation on mercury emission from coal-fired power generation on March 15, 2005 [4]. As specified in the rule, the mercury emission from utility boilers will have to be reduced to a final cap at 15 ton/year in 2018. Coal is a more important energy source in China than it is in America. China also pays more attention to mercury emissions and sponsors the projects relative to the mercury emission control [5].

During combustion, the mercury (Hg) in coal is volatilized and converted to elemental mercury (Hg^0) vapor in the high temperature regions of coal-fired boilers. As the flue gas is cooled, a series of complex reactions begin to convert Hg^0 to oxidized mercury (Hg^{2+}) compounds and/or Hg compounds (Hg^p) that are in a solid-phase at flue gas cleaning temperatures or Hg that is adsorbed onto the surface of other particles. This partitioning of Hg into Hg^0 , Hg^{2+} , and Hg^p is known as mercury speciation, which can have a considerable influence on selection of mercury control and measuring methods [6]. Compared with Hg^0 , Hg^{2+} and Hg^p are more effectively captured in conventional air pollution control devices (APCD) (such as wet flue gas desulphurization, electrostatic precipitators, and fabric filters, etc.) and are more apt to deposit locally or regionally. Mercury emission control efficiencies for coal-fired boilers can be improved by fuel blending, APCD configuration and its operating con-

ditions [7]. In this paper, mercury concentration and speciation partitioning, including Hg^T (total Hg including Hg^0 , Hg^{2+} and Hg^p), Hg^0 , and Hg^{2+} from two lignite-fired power plants under different operating conditions, was studied by Ontario hydro method, semi-continuous emission monitors, continuous mercury monitor and the sorbent trap method. The effects of boiler load, fuel blending ratio, ESP, FGD, flue gas bypassing the FGD ratio, and mercury measuring methods on mercury emissions were analyzed.

EXPERIMENTAL

1. Utility Boiler APCD Configuration and Sampling Location

The details of the tested 2 boilers' configuration are given in Table 1. The air pollution control devices' configuration and sampling location in power plant 2 are shown in Fig. 1. The analyses of tested Taxes lignite and PRB bituminous coal are shown in Table 2. The blending coals with 57/43 and 91/9 of Taxes lignite/PRB bituminous coal were fired in power plant 1 and power plant 2, respectively.

2. Test Methods

Four kinds of Hg measurements were carried out during the testing, which includes Ontario hydro method, PS Analytical Sir Galahad analyzer, Horiba Hg-continuous mercury monitor, and the sorbent trap method. Mercury in coal collected from feeders and ash samples collected from the dust collector, ESP, and/or OHM filter are analyzed with the Leco advanced mercury analyzer 254 (AMA 254). The AMA 254 is cold vapor atomic absorption (CVAA) instrument. The AMA 254 has a detection limit of 0.01 ng and a detection range of 0.05-600 ng [8].

2-1. Ontario Hydro Method

The Ontario hydro Method is a standard method for measuring and speciating mercury in flue gas [9]. OHM has two possible configurations based on EPA Methods 5 and 17, out-of-stack filtration and in-stack filtration, respectively [8]. A sample is withdrawn from the flue gas stream isokinetically through the filtration system, which

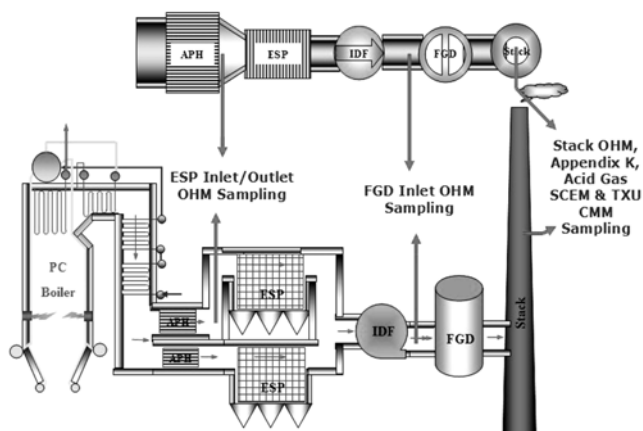
[†]To whom correspondence should be addressed.

E-mail: luping@njnu.edu.cn

[‡]This work was presented at the 7th China-Korea Workshop on Clean Energy Technology held at Taiyuan, Shanxi, China, June 26-28, 2008.

Table 1. Information of onsite tested utility boilers

Power plant	Boiler type	Lignite/ PRB coal	Power capacity (MWe)	PM control device	ESP inlet temperature (°C)	FGD	Remark
Power plant 1	Front-wall fired PC boiler with low NO _x burner	57/43	560	Cold-side ESP in parallel with baghouse=40/60	211	None	NH ₃ injection before ESP
Power plant 2	Front-wall fired PC boiler with low NO _x burner	91/9	860	Cold-side ESP	183	Wet FGD	Flue-gas bypass FGD

**Fig. 1. APCD configuration and sampling locations in power plant 2.**

is followed by a series of impingers in an ice bath. Particulate-bound mercury is collected on the filter; oxidized mercury is collected in the first three impingers containing 1.0 N potassium chloride (KCl) solution; elemental mercury is collected in one impinger containing a 5% nitric acid (HNO₃) and 10% peroxide (H₂O₂) solution and in three impingers containing a solution of 10% sulfuric acid (H₂SO₄) and 4% potassium permanganate (KMnO₄). An impinger containing silica gel collected any remaining moisture. The filter media consisted of quartz fiber filters. An approximate 2-hour sampling time was used, with a target sample volume of 1 to 2.5 standard cubic meters. The OHM solutions were analyzed with a Leeman Labs Hydra AA. The Hydra AA is a cold vapor atomic absorption (CVAA) instrument dedicated to mercury analysis.

2-2. Semi-continuous Emissions Monitor

The semi-continuous emissions monitor (SCEM), which uses a gold trap to collect mercury from the flue gas before analysis with an atomic fluorescence detector, is manufactured by PS Analytical [9]. The PS Analytical Sir Galahad analyzer consists of four major components: (1) A probe, filter, and pump module; (2) Heated Teflon sample lines, which are normally kept at >120 °C and are needed to prevent losses of Hg along the sample lines, as well as to keep the speciation the same as that in the stack, and to reduce condensation of acid gases; (3) The stream selection and Hg conversion system, which splits the incoming flue gas into two streams. One stream passes through a KCl solution, which removes oxidized mercury, thereby allowing only elemental mercury to reach the detector. The other stream passes through a stannous chloride (SnCl₂) solution, which reduces oxidized mercury to Hg⁰, thus facilitating in the measurement of the total mercury. Both solutions also serve the dual purpose of removing acidic gases that could damage the gold detector; and (4) The analyzer and data processing system. The SCEM system also has an Hg vapor generator capable of supplying a constant stream of Hg vapor (about 14 l/min) for calibration purposes.

2-3. Horiba/NIC DM-6B Continuous Mercury Monitor

The Horiba/NIC DM-6B is essentially two DM-6 “dry” units running in parallel. These two units are intended for separating the mercury contained in the flue gas of coal-fired and municipal waste incineration utilities into gaseous elemental mercury and oxidized mercury, and then continuously measuring these two types of mercury by using a dual absorption-cell system [10]. In the first unit, the sampling gas is drawn from the stack and passes through a filter to remove dust. The mercury compounds are then reduced to Hg⁰ by contacting with the solid-state reduction catalyst which is housed

Table 2. Proximate analyses and ultimate analyses of tested Coals

Coal sample	Proximate analysis			Ultimate analysis					Chloride mg/kg	Mercury mg/kg	Heating value Q _{net,d} MJ/kg	Ratio of lignite to PRB %
	M _{ar} %	V _{daf} %	A _d %	C _d %	H _d %	S _d %	N _d %	O _d %				
Lignite 1	20.43	29.03	19.57	41.08	5.68	0.49	0.92	32.27	100	0.18	15.97	57/43
PRB 1	8.16	35.09	8.80	54.85	6.04	0.37	0.57	29.38	148	0.18	21.60	
Lignite 2	16.98	29.27	21.80	43.44	5.23	0.56	0.93	28.04	145	0.24	16.83	57/43
PRB 2	7.16	35.07	9.79	54.28	5.94	0.34	0.58	29.07	134	0.08	21.62	
Lignite 3	22.51	32.46	13.29	47.65	5.89	1.10	1.02	31.05	102	0.13	19.60	91/9
PRB 3	7.19	41.67	10.00	61.95	4.90	0.61	1.11	21.43	<100	0.09	24.26	
Lignite 4	16.64	33.15	18.83	48.62	5.30	1.61	1.02	24.62	134	0.18	19.20	91/9
PRB 4	9.70	41.74	7.61	61.70	5.12	0.45	0.80	24.32	101	0.06	24.04	

in the probe. The sample gas with the reduced elemental mercury then passes through a chiller to remove the moisture (condensate is continuously pumped back into the stack) and then it is transported to the detector via Teflon tubing to be continuously measured by CVAA. In the second unit, the sampling flue gas passes through a chiller before contacting with the catalyst. By doing this, the oxidized mercury is removed with the condensate, and a measurement of the gaseous elemental mercury in the sampling gas stream is obtained. A liquid crystal display shows the mercury concentration, which is updated every second. The detector unit has outputs for either an external computer and/or a data logger. The response time is less than 1 minute, and the sensitivity is listed as $0.1 \mu\text{g}/\text{m}^3$. The advantages of Horiba CMM are that it is more portable, needs fewer power requirements, costs less, and no requirement of gold trap or

argon. But due to the dry catalyst used, it has some disadvantages, such as catalyst life and limitation, requirement of the addition of HCl, and the selenium problem.

2-4. Sorbent Trap Method (40 CFR, Part 75, Appendix K/EPA Method 324)

Appendix K (or EPA method 324) is for the continuous sampling of mercury emissions in combustion flue gas streams with sorbent traps [11]. A schematic of a single trap sampling train, which includes sorbent traps, a sampling probe, a heated umbilical vacuum line, a moisture knockout, a vacuum pump, and a dry gas meter, is shown in Fig. 2. Known volumes of flue gas are extracted from a duct through single or paired sorbent traps with a nominal flow rate of 0.2–0.6 l/min through each trap. Each trap is then acid leached and the resulting leachate is analyzed by a cold vapor atomic fluores-

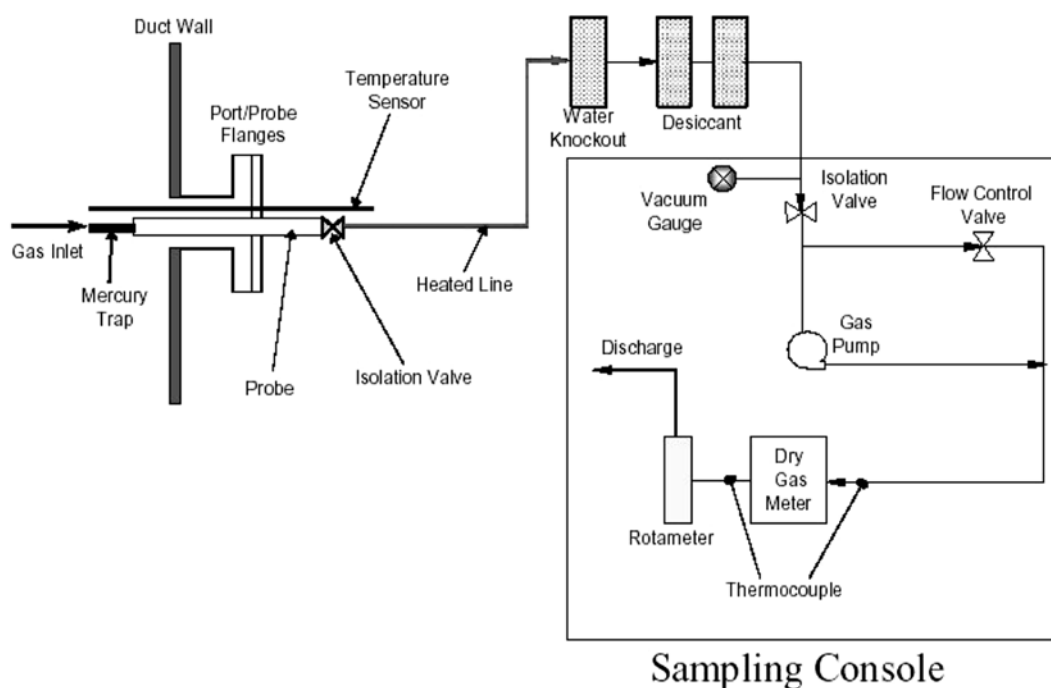


Fig. 2. A schematic of the sorbent trap sampling train.

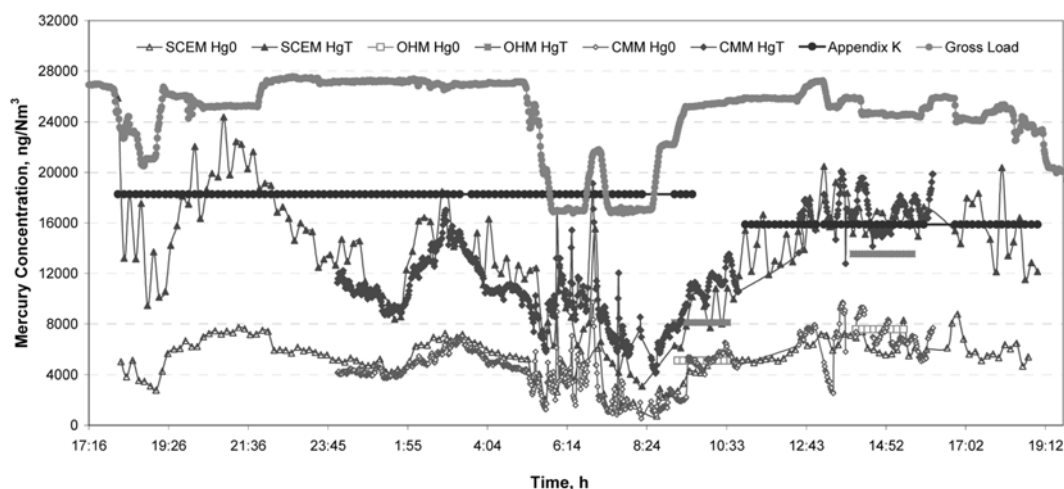


Fig. 3. The correlations amongst the data trends by four measuring methods in power plant 1.

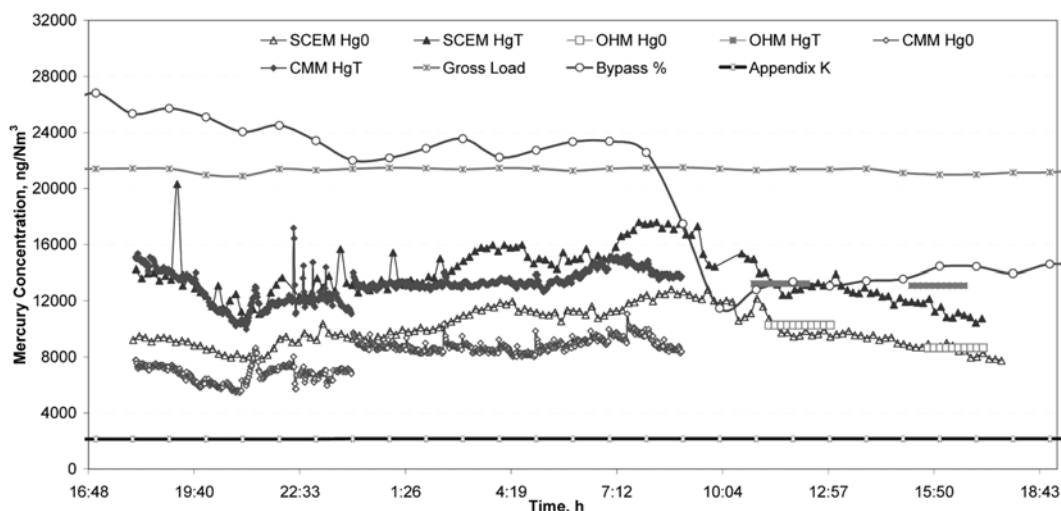


Fig. 4. The correlations amongst the data trends by four measuring methods in power plant 2.

cence spectrometer (CVAFS) or by a cold vapor atomic absorption spectrometer (CVAA).

RESULTS AND DISCUSSION

1. The Effects of the Mercury Measurements on Mercury Emission

The mercury emissions by four measurements of OHM, CMM, SCEM, and Appendix K in power plant 1 and power plant 2 are shown in Fig. 3 and Fig. 4, respectively. In power plant 1, the averaged boiler load was 379 MWe with a standard deviation of 7 MWe, the NH_3 injection before the ESP inlet was about 4.08 kg/h, and the blending ratio of Taxes Lignite and PRB bituminous coal was 57%/43%. In power plant 2, the averaged boiler load was 852 MWe with a standard deviation of 3 MWe, the percentage of flue gas bypassing the FGD was 15-22%, and the blending ratio of Taxes Lignite and PRB was 91%/9%. SO_2 removal efficiency is larger than 95% based on the measured SO_2 concentrations at the inlet and outlet of FGD. As the Figures show, the data from SCEM and CMM show the same trends, which were consistent with the boiler load trend. The data from two continuous mercury monitors (SCEM and CMM) show a good consistency with OHM data during the test. However, there are big discrepancies between the data from Appendix K and that from methods of SCEM, CMM, and OHM. Compared with the testing results in Fig. 3 and Fig. 4, the CMM provided valid and representative Hg^T data and the little lower Hg^0 data than that from the OHM and SCEM during most of the tested time. All these indicated that (1) the mercury emission generation in the flue gas was closely related to the release of the mercury content in coal caused by fuel consumption during the combustion process; (2) the catalysts used in CMM Hg measurement and the carbon used in sorbent trap method became contaminated very easily due to some of chemical compounds in the flue gas, namely, selenium. So, the lifetime of the CMM catalysts and sorbent traps really presents some challenges for long-term mercury monitoring.

2. The Effects of Mercury Measurements on Mercury Speciation

Fig. 5 shows the result of mercury speciation at the stack from Hg

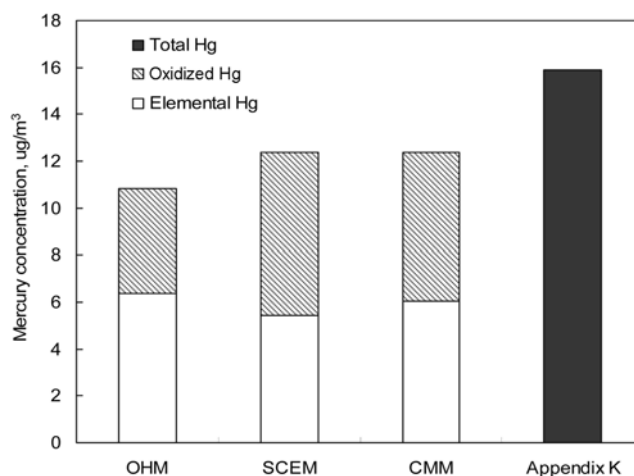


Fig. 5. Mercury speciation at stack by four-method measurements in power plant 1.

measurements of OHM, SCEM, CMM, and Appendix K in power plant 1. The Hg data from CMM, Appendix K and SCEM testing was used to compare with the OHM Hg data. As can be seen, the percentage of elemental mercury was in the range of 43.9-58.6% by different methods. The mercury data from OHM, SCEM and CMM presented a good consistency throughout the entire testing period within $\pm 20\%$ acceptable range. For example, the differences in Hg^0 and Hg^T between the OHM and the SCEM were -17.1% and 12.3% , respectively; the differences between the OHM and CMM in Hg^0 and Hg^T were -5.5% and 20.0% , respectively. However, the difference in Hg^T between OHM and Appendix K was 31.7% . The cause of higher discrepancies between the Hg^T results of OHM and Appendix K might be the fluctuation of boiler load as shown in Fig. 3.

The mercury speciation amongst OHM, SCEM and appendix K at a stack in power plant 2 is shown in Fig. 6. The percentage of elemental mercury was 71.9% and 74.2% by OHM and SCEM, respectively. The differences in Hg^0 and Hg^T between the OHM and the SCEM were -3.5% and 3.6% , respectively. However, combined with Fig. 5, the appendix K results were about 300-500% lower

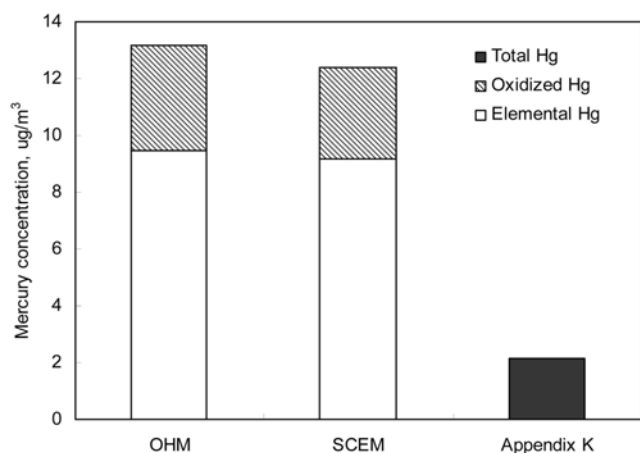


Fig. 6. Mercury speciation at stack by OHM, SCEM, and Appendix K in power plant 2.

Table 3. The selenium analyses from the fuel and ash samples (mg/kg)

Power plant No.	Se in fuel	Se in ash	Se in slurry	Se in flue gas	TX lignite/PRB
Power plant 1	2.4	1.0	-	1.4	57%/43%
Power plant 2	4.4	0.6	0.1	3.7	91%/9%

than the average of OHM and the other data from two continuous mercury monitors. The possible reason is that some minor metals (such as selenium) prevented the vapor phase mercury from being captured by the carbon inside the traps, thus biasing the testing results. It is known that selenium species in the vapor phase would poison some mercury treatment catalysts. This is quite common because the carbon traps capture mercury with their active sites on the surface area through gas-solid phase reactions. If these sites are covered up by other chemical compounds, then there will be no room left to absorb mercury.

The selenium analyses from the fuel and ash samples are shown in Table 3, which indicates the selenium in the flue gas at power

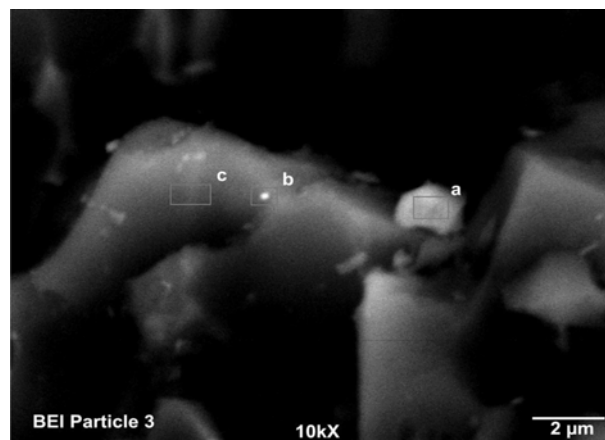


Fig. 7. Microstructure of the Appendix K carbon trap particles.

plant 2 is higher than that at power plant 1. The scanning electron microscope (SEM) picture taken from one of the Appendix K carbon traps in power plant 2 is shown in Fig. 7. As the figure shows, many of the Se particles (white particles) were identified on the surface of carbon particles. Therefore, the bias between the Hg^T results might be due to the big discrepancies for selenium in the flue gas at these two power plants. The results also indicate that the fuel blending could be a powerful tool to control any targeted chemical contents in the fuel (such as mercury, selenium, etc.). As Table 1 and Table 3 show, PRB coal generally contains lower mercury and selenium content than Texas lignite; thus a proper fuel blending ratio between the two fuels that produces required heat output could also minimize unwanted air pollutant emission.

As for the CMM method, due to the possible selenium contamination on the surface of its Hg^T and Hg^0 conditioning catalysts, it is observed that the catalysts had to be replaced every three to four days. Besides, the Hg^0 data sometimes could vary more than 50% from the OHM data and the SCEM data.

3. The Effects of Boiler Configuration and Operating Conditions on Mercury Removal Efficiency

Mercury removal efficiency is based on a combined functional-

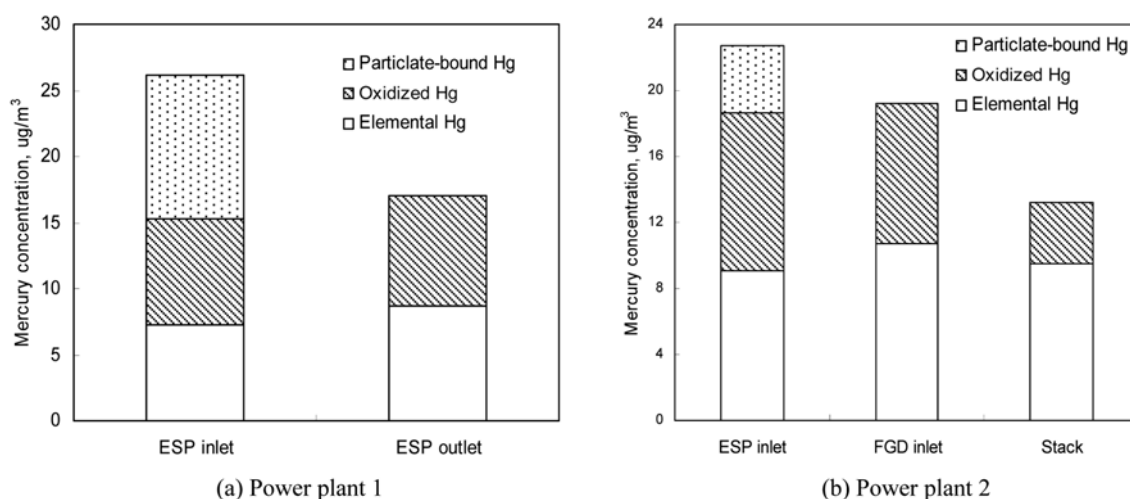


Fig. 8. Mercury speciation by the OHM method in two power plants.

ity of temperature change across the air-preheater (APH), acid gaseous content (such as halogen), fly ash reactivity and surface area, and other trace metal effects [12]. Normally, after the flue gas travels through the APH, the mercury oxidization formation is complete when the temperature decreases from the inlet at approximately 370 °C to the outlet at approximately 140 °C. As is well known, a lower temperature at the APH outlet increases the chances for mercury oxidization and formation of particulate-bound mercury. So, the oxidized mercury binds in the fly ash and is captured by the ESP or baghouse. Fig. 8 shows the mercury speciation at ESP, FGD, and stack by the OHM method in two power plants. It is observed that the particulate-bound mercury species in power plant 1 and power plant 2 were 41.6% and 17.9%, respectively. As the flue gas flowed across the ESP, the fly ash in the flue gas absorbed the particle-bound mercury and yielded Hg control efficiencies of 35% in power plant 1 and 15% in power plant 2, respectively. The higher mercury removal efficiency in power plant 1 is partly due to ammonia (NH₃) injection before the ESP inlet, which enhanced the fly ash conductivity and resulted in the mercury control efficiency due to increasing the amount of particulate-bound mercury. The elemental mercury species in vapor phase at the ESP inlet in power plant 1 and power plant 2 were 47.5% and 49.6%, respectively. As Table 2 shows, the ESP inlet temperature of power plant 1 and power plant 2 were 211 °C and 183 °C, respectively. Due to the higher temperature environment at ESP inlet, mercury oxidization was inhibited and resulted in the higher elemental mercury species in the flue gas.

Generally speaking, the post-combustion systems equipped with a FGD would wash off more than 95.0% of SO₂, and at the same time capture more than 90% of oxidized mercury because both pollutants are water soluble. By comparing the Hg^T across the FGD in Fig. 8(b), the Hg²⁺ removal efficiency was about 60.0%, and around 28% of Hg²⁺ was emitted into the ambient atmosphere. This is due to an average of 16% of the flue gas bypassing the FGD during the testing. So, in order to obtain a higher mercury removal efficiency, the ESP inlet temperature and the percentage of flue gas bypassing the FGD should be decreased. All these will increase the percentage of oxidized mercury and the chance of flue gas being treated through the FGD.

CONCLUSIONS

1. Four-method mercury measurement of OHM, SCEM, CMM, and appendix K was carried out in two lignite-fired power plants. Mercury emissions data from OHM, SCEM and CMM presented a good consistency throughout the entire testing period within ±20% acceptable range.

2. The data from Appendix K produced bigger discrepancies than

the results from the OHM and SCEM due to the selenium interferences. The lifetime of the CMM catalysts and sorbent traps presents some challenges for long-term mercury monitoring.

3. At the same level of total mercury emission the elemental mercury emissions at stack in two lignite-fired plants was in the higher ranges of 43.9-74.2%.

4. The particulate-bound mercury removal efficiencies of ESP were determined to be 16-35% in two lignite-fired power plants. The wet flue gas desulphurization would capture more than 90% of oxidized mercury.

ACKNOWLEDGMENTS

This financial support of the Natural Science foundation of Jiangsu Province of China (BK2007532) and the Natural Science Foundation of the Jiangsu Higher Education Institutions of China (07KJD610119) is gratefully acknowledged.

REFERENCES

1. US EPA. Report 453/R-98-004a, *A study of hazardous air pollutants from electric utility steam generating units: final report to congress* (1998).
2. US EPA Report 452/R-97-003, *Mercury study report to congress* (1997).
3. R. Yan, D. T. Liang and J. H. Tay, *Environ. Sci. Pollut.*, **10**, 399 (2003).
4. US EPA, *Clean air mercury rule*, Available from: <http://www.epa.gov/mercuryrule> (2005).
5. X. Yang, Y. Zhuo, Y. Duan, L. Chen, L. Yang, L. Zhang, Y. Jiang and X. Xu, *Korean J. Chem. Eng.*, **24**, 711 (2007).
6. K. C. Galbreath and C. J. Zygarlicke, *Fuel Processing Tech.*, **65-66**, 289 (2000).
7. A. Kolker, C. L. Senior and J. C. Quick, *Applied Geochemistry*, **21**, 1821 (2006).
8. S. Kellie, Y. Duan, Y. Cao, P. Chu, A. Mehta, R. Carty, K. Liu, W. Pan and J. T. Riley, *Fuel Processing Tech.*, **85**, 487 (2004).
9. ASTM, *Standard test method for elemental, oxidized, particulate-bound, and total mercury in flue gas generated from coal-fired stationary source (Ontario Hydro Method)*, Designation: **D 6784-6702**.
10. D. L. Laudal, *MEC2 2nd International expert's workshop*, Ottawa, Canada (2005).
11. US EPA. *Electronic code of federal regulations Title 40-Protection of environment, Part 75: Appendix K*, Available from: <http://ecfr.gpoaccess.gov/>.
12. Y. E. Yudovich and M. P. Ketris, *International Journal of Coal Geology*, **62**, 135 (2005).