

In-situ measurement and distribution of flue gas mercury for a utility PC boiler system

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Abstract: The in-situ instrumentation technique for measuring mercury and its speciation downstream a utility 100 MW pulverized coal (PC) fired boiler system was developed and conducted by the use of the Ontario hydro method (OHM) consistent with American standard test method together with the semi-continuous emissions monitoring (SCEM) system as well as a mobile laboratory for mercury monitoring. The mercury and its speciation concentrations including particulate mercury at three locations of before air preheater, before electrostatic precipitator (ESP) and after ESP were measured using the OHM and SCEM methods under normal operation conditions of the boiler system as a result of firing a bituminous coal. The vapor-phase total mercury Hg(VT) concentration declined with the decrease of flue gas temperature because of mercury species transformation from oxidized mercury to particulate mercury as the flue gas moved downstream from the air preheater to the ESP and after the ESP. A good agreement for Hg⁰, Hg²⁺ and Hg(VT) was obtained between the two methods in the ash-free area. But in the dense particle-laden flue gas area, there appeared to be a big bias for mercury speciation owing to dust cake formed in the filter of OHM sampling probe. The particulate affinity to the flue gas mercury and the impacts of sampling condition to accuracy of measure were discussed.

Key words: coal fired flue gas; mercury speciation; in-situ measurement; Ontario hydro method (OHM); semi-continuous emissions monitoring (SCEM)

Coal combustion is the primary source of anthropogenic mercury emissions in worldwide atmosphere surroundings, accounting for 72 of 158 t/a of total point-source mercury emissions in USA^[1], and average of 138 t/a in China with an annual ever-increasing rate of 4.8%^[2]. Investigation into physical and chemical interactions and transformations of mercuric compounds downstream flue gas flow of pulverized coal (PC) fired boiler system is imperative for understanding the formation, transportation and speciation of mercury released into air pollution control systems and the atmosphere. The current knowledge of mercury transformations in coal combustion flue gas is largely based on thermodynamic modeling and experimental investigation of mercury reactions in simulated flue gases and, to a limited extent, on the interpretations of field test data^[1]. However, quantitative prediction of the emissions of specific mercury species from coal-fired power plants can still not be made^[3]. Field-testing is

highly necessary for determining the mechanism of mercury speciation, transformation and modeling.

Mercury exists primarily as gaseous elemental mercury, Hg⁰(g), and as gaseous or solid(s) inorganic mercuric compounds, Hg²⁺X (e. g., where X is Cl₂(g), SO₄(s), O(s, g), S(s)), in coal combustion flue gas^[1]. Mercury emissions from coal-fired boilers can be empirically classified into three main forms: Hg⁰(g), Hg²⁺X(g), and Hg(p). Oxidized mercury is soluble in water and has a tendency to associate with particulate matter, whereas elemental mercury is volatile, insoluble in water, and has a very high vapor pressure at the operating temperatures of typical particulate control devices. The major problem for mercury control systems is both converting as much elemental mercury into oxidized ones, which then can easily be captured by air pollution control devices (APCD) and capturing the water-insoluble elemental mercury, which is identified as the hazardous air pollutant of the greatest potential public health concern.

In this paper, a utility 100 MW coal fired PC boiler was chosen to carry out the field test measurement and detect the mercury and its speciation emissions downstream the flue gas flow from air preheater (APH) to ESP. The OHM and SCEM systems were

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both used to better understand the transformation and speciation of mercury in coal combustion flue gas. The mercury in flue gas was trapped in chemical solutions of the OHM sampling train, which was analyzed using the Leeman Hydra AA with Leeman Hydra Prep. The flue gas samples were also analyzed by the PS analytical SCEM system at the same time for making contrast between these two methods and for data validation. Mercury speciations at three locations (prior to APH, before the dust collector and after ESP) were detected and discussed.

1 Instrumentation

1.1 Mobile laboratory for mercury monitoring

Western Kentucky University (WKU) is one of the five laboratories (Philips, EERC, Consol and Test America) in North America capable of conducting the SCEM and OHM in situ for mercury emissions in power plants. A mobile (53-foot-long) laboratory was designed, constructed at WKU and has been used at power plants for mercury measurements and analyses on site. It is equipped with an analytical room, an OHM chemical solution preparation room, and a stock room for storing various probes, glass wares, instruments, and other appliances, as described in Ref. [4]. The mercury sampling, recovery, digestion and concentration analysis can be fulfilled at once in this mobile laboratory. There is no interruption in the power plant operation when conducting the samples and analyses for mercury field tests.

1.2 Ontario hydro method for mercury speciation

The ASTM for mercury analysis was applied and the versatile Apex instruments specific isokinetic sampling train including probe with heated glass liner, heated filter box, EPA method 5 glassware set, and metering console were used. This system permits traversal sampling of either vertical and lateral points or space-limited locations. After sampling, solutions will be recovered, digested and mercury detected using a Leeman Hydra AA and Hydra Prep automated mercury analysis system. This mercury analyzer is a fully compliant, automated mercury analyzer employing a dual beam, cold vapor atomic absorption (CVAA) system. This system features a detection limit of mercury at 1 part per trillion.

1.3 PS analytical mercury SCEM system

The system consists of four major components: ① A probe, filter and pump module; ② Heated Teflon sample lines, which are normally kept at 200 °C and are needed to prevent losses of Hg along the sample

lines and to keep the speciation the same as that in the stack, and to reduce condensation of acidic gases; ③ The Hg conversion system; ④ The analyzer, Sir Galahad, and data treatment system.

The system also contains an Hg vapor generator for calibration. This device is able to supply a constant stream of Hg vapor and blank at typically 14 L/min. These gases go through the valve-switching box and can be directed to the probe to completely check the system bias. One unique feature of the SCEM system in this field test is that it has two speciation modules attached into one analyzer, which allows it to detect Hg from two separate points at the same time, i. e. before and after ESP. An ash-free probe for sucking dust laden flue gas was applied at the pre-ESP location for feeding clean flue gas into the speciation module where Hg^0 and Hg^{2+} are partitioned. A conventional sampling probe, provided by PS analytical Co., was used at the post-ESP location, which is favored for sucking ash-free flue gas.

2 Result and Discussion

The field test and measurement aimed at two main tasks. The first was to investigate the actual mercury emissions and their profile downstream the rear flue gas duct in the selected PC boiler system through the APH, dust collector (DC) and ESP, which was strongly dependent upon flue gas temperature, coal composition, flue gas cleanup system, and operating conditions of coal combustion^[5]. The second was to compare the measurement results obtained by the OHM and SCEM methods and validate the mercury emission data from a utility PC boiler system so that it was available to provide the database for further study on mercury emission and control. For both tasks, three mercury sampling locations were installed to collect flue gas samples with a particulate filter in the probe downstream boiler exit till the ESP outlet. They are pre-APH, before the air preheater with a flue gas temperature at 343 °C; pre-ESP, before the dust collector and ESP at 149 °C and post-ESP, after ESP at 140 °C. The OHM is used for all the three ports. The Hg SCEM system is used only before and after ESP sampling ports at the same time. So, the measurement data of OHM and SCEM are able to check each other in the Hg emission monitoring system. During the field test, most operation parameters of the boiler system run steadily. The average analytical data of the feeding coal to the boiler are listed in Tab. 1.

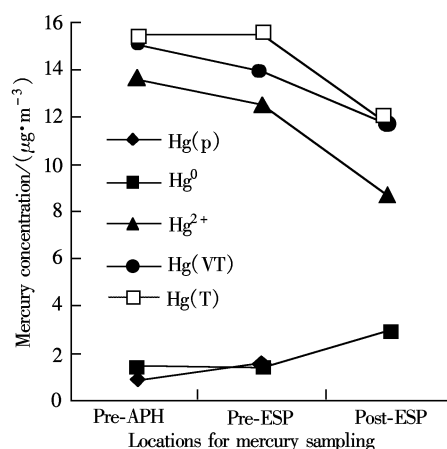
Tab. 1 Average analysis data of the feeding coal (air dry basis)

Approximate analysis/%				Ultimate analysis/%					Trace element/ 10^{-6}	
w(W)	w(A)	w(V)	w(FC)	w(C)	w(H)	w(N)	w(S)	w(O)	Hg	Cl
2.63	9.60	32.89	54.88	75.79	5.00	1.77	1.30	3.91	0.12	1.006

2.1 Mercury result from OHM method

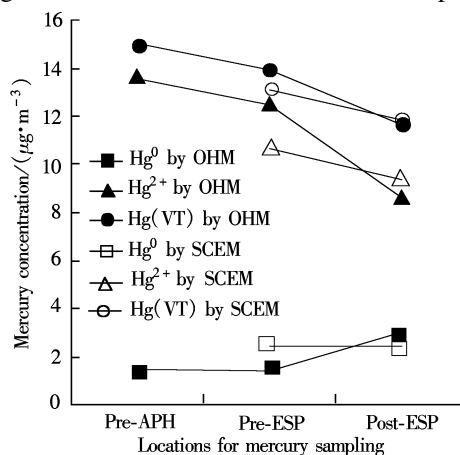
The measured mercury concentrations varied through the APH to ESP from OHM method is shown in Fig. 1 in terms of particulate mercury $\text{Hg}(p)$, gaseous elemental mercury Hg^0 , gaseous oxidized mercury Hg^{2+} , vapor-phase total mercury $\text{Hg}(\text{VT})$ sum of Hg^0 and Hg^{2+} , and total mercury $\text{Hg}(\text{T})$ sum of all the above mercury species. It is well known that when coal is burnt in the high temperature PC boiler, all the mercury in coal will be converted into gaseous elemental mercury Hg^0 at temperatures of over 800°C that mixes with the flue gas^[6]. With the ever decreasing of the gas temperature, some of Hg^0 will react with ionic Cl^- , atomic Cl-Cl , O-O and S in the flue gas and form mercuric compounds such as HgCl , Hg_2O , HgS , Hg_2SO_4 , and so on. Some of Hg^0 and Hg^{2+} will be adsorbed onto surface of char or fly ash particles and form particulate mercury $\text{Hg}(p)$. While there is still some amount of Hg^0 remaining in the flue gas. The mechanisms of the mercury's transfer, conversion, transportation, adsorption and desorption are not very clear now. They are strongly dependent on the type of coal, combustion temperature, chemical reaction conditions, flue gas components and fly ash constituents. For the selected 100 MW PC boiler system at its rated operation condition, it can be seen from Fig. 1 that with the decrease of the flue gas temperature when going out of the boiler exit through the APH, pre-ESP to post-ESP locations, the particulate mercury $\text{Hg}(p)$ is formed and tends to increase from APH to pre-ESP because of reduction of the oxidized mercury, which means more Hg^{2+} than Hg^0 is converted into $\text{Hg}(p)$. As a result, the vapor-phase mercury $\text{Hg}(\text{VT})$ is reduced owing to reduction of Hg^{2+} . While the total mercury $\text{Hg}(\text{T})$, sum of all the gaseous and particulate mercury in the flue gas, remains constant from APH to pre-ESP with only a little mercury loss as deposited ashes in the duct, which represents the mercury balance in the whole system. $\text{Hg}(\text{T})$ is lowered from pre-ESP to post-ESP because no fly ash is collected at the post-ESP point, the reduction of $\text{Hg}(\text{T})$ will be balanced by the $\text{Hg}(p)$ collected at the dust collector (DC) and ESP ashes. According to the actual data, a maximal vapor-phase mercury $\text{Hg}(\text{VT})$ concentration of $15.053\ \mu\text{g}/\text{m}^3$ at the pre-APH location was detected at a flue gas temperature of 343°C . That value decreased to $13.909\ \mu\text{g}/\text{m}^3$ at the pre-ESP point of 149°C and $11.648\ \mu\text{g}/\text{m}^3$ at the post-ESP

point of 140°C . The vapor phase total mercury concentration in flue gas decreases gradually because of mercury species transformation from the oxidized phase to particulate phase^[7,8]. This transformation also leads to changes in mercury speciation.

**Fig. 1** Mercury speciation downstream PC boiler measured by OHM method

2.2 Mercury result from SCEM method

In contrast to OHM analysis, the Hg SCEM system has the advantage of monitoring mercury emissions on-line. The measurement of mercury concentration for both methods was conducted in the same test period so that the data could be compared each other. The time averaged mercury speciation from SCEM is shown in Fig. 2 in the background of results from OHM. The measured Hg^{2+} and $\text{Hg}(\text{VT})$ by SCEM show similar trends contrasted to the results by OHM, in which they decrease when going through the DC and ESP, except that Hg^0 shows a slight change only. During the on-line measurement of SCEM process, it

**Fig. 2** Comparison of mercury speciation measured by OHM and SCEM methods

is observed that both instantaneous and time-averaged vapor-phase mercury concentration at the pre-ESP point is always higher than that at the post-ESP point, which is reasonable and reflects the fact that some of gaseous Hg^{2+} is converted into $\text{Hg}(\text{p})$ that is adsorbed on the particulate surfaces trapped in the DC and ESP.

2.3 Comparison between OHM and SCEM methods

For the elemental mercury emitted out of ESP to the atmosphere, the OHM shows Hg^0 of $3.023\text{ }\mu\text{g}/\text{m}^3$ and SCEM $2.460\text{ }\mu\text{g}/\text{m}^3$ with a bias of 12.67% as shown in Tab. 2. For the vapor-phase total mercury at post-ESP point, those two methods show numbers of $11.648\text{ }\mu\text{g}/\text{m}^3$ and $11.844\text{ }\mu\text{g}/\text{m}^3$ respectively, with a small bias of 1.6%. There is a good agreement for Hg^0 and $\text{Hg}(\text{VT})$ after ESP between these two methods.

Tab. 2 Comparison of mercury speciations between OHM and SCEM methods

Methods	Locations	$\rho(\text{Hg}^0)/(\mu\text{g}\cdot\text{m}^{-3})$	$\rho(\text{Hg}^{2+})/(\mu\text{g}\cdot\text{m}^{-3})$	$\rho(\text{Hg}(\text{VT}))/(\mu\text{g}\cdot\text{m}^{-3})$	$\text{Hg}^0/\text{Hg}(\text{VT})$	$\rho(\text{Hg}(\text{p}))/(\mu\text{g}\cdot\text{m}^{-3})$
OHM	Per-ESP	1.416	12.492	13.909	0.1018	1.575
	Post-ESP	3.023	8.625	11.648	0.2596	0
SCEM	Per-ESP	2.443	10.663	13.106	0.1841	N/A
	Post-ESP	2.460	9.384	11.844	0.2050	N/A

The comparison of mercury speciation, the ratio of Hg^0 to $\text{Hg}(\text{VT})$, between OHM and SCEM measured before and after ESP are illustrated in Fig. 3. However, it shows a bigger bias than that of Hg^0 and $\text{Hg}(\text{VT})$, especially at the pre-ESP location. The SCEM detects a relatively stable mercury speciation of 18.4% and 20.5% at pre-ESP and post-ESP points. While the OHM indicates 10.2% and 25.9% respectively at both locations. The reason is that they use a distinct type of sampling probe. The OHM probe has a dust-filter at its tip where the fines are separated from the flue gas and are subject to form a dust-cake stuck to the filter wall. The flue gas must penetrate into this dust-cake first before going out from it. So, the fly ash dust-cake acts as a sorbent which has the potential to capture mercury in the flue gas and thus make the mercury speciation varied^[9]. The SECM probe utilized in this test is an innovative ash-free-probe in which a tube filter is installed and compressed air is used to suck the flue gas. Its unique feature is that the flue gas is separated from the dust flow by its smaller inertial force than particulate so that the gas sample is more representative without adsorption as occurred in the dust cake.

Tab. 2 lists the measured data in detail by the OHM and SCEM methods at the locations of pre-ESP and post-ESP respectively. At the post-ESP point, only a gaseous sample is collected in the flue gas for both

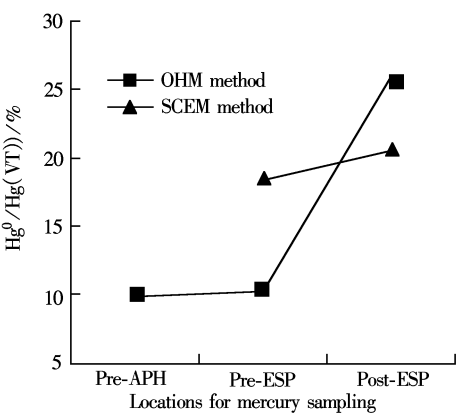


Fig. 3 Comparison of $\text{Hg}^0/\text{Hg}(\text{VT})$ measured by OHM and SCEM methods

OHM and SECM sampling because there is no fly ash sample trapped in the OHM tip filter. So, the data by both methods are comparable and are found matchable. However at the pre-ESP point that is located across the DC and ESP to the post-ESP point and an area being full of particle-laden flue gas, there appears to be a big bias between these two methods. The dust collected in the OHM tip filter shows an equivalent mercury concentration of $1.575\text{ }\mu\text{g}/\text{m}^3$ for $\text{Hg}(\text{p})$ and a gaseous mercury concentration of only $1.416\text{ }\mu\text{g}/\text{m}^3$ for Hg^0 . The Hg^0 by SCEM is $2.443\text{ }\mu\text{g}/\text{m}^3$ much bigger than that of OHM figure. That is why the mercury speciation at the pre-ESP point by OHM and SCEM is quite different. In fact, mercury collected on the OHM sampling filter with the fly ash is considered to represent the affinity of the specific fly ash to mercury but not necessarily the amount of mercury on the particulate at that location^[9]. Or there must be some physical and/or chemical adsorption that occurred when the flue gas dust is depositing on the filter wall and is forming the dust-cake when flue gas is leaching. In particle-laden flue gas, the OHM can distinguish the particulate mercury speciation, but the SCEM can better distinguish the gaseous mercury speciation. In the cleaned or ash-free flue gas, both OHM and SCEM provide consistent mercury speciations.

3 Conclusions

1) Combining the mercury OHM with SCEM for field measurement and analyses on flue gas mercury, its speciation in a utility boiler system in situ has been successful in the newly built Western Kentucky University mobile laboratory for mercury emission monitoring. The total mercury vapor-phase concentration declined with the ever decreasing of flue gas temperature because of mercury species transformation from oxidized mercury to particulate mercury as the flue gas moves downstream from the air preheater to the

ESP and after the ESP.

2) The measured Hg^0 , Hg^{2+} and $\text{Hg}(\text{VT})$ by SCEM display similar trends varying from the pre-ESP to post-ESP, except for Hg^0 which shows a slight change contrasted to the results by OHM. During the on-line measurement of the SCEM process, it can be found that the vapor-phase mercury concentration at the pre-ESP point is always higher than that at the post-ESP point, which is reasonable and reflects the fact that some of gaseous Hg^{2+} is converted into $\text{Hg}(\text{p})$ that is adsorbed on the particulate surfaces trapped in the DC and ESP.

3) The measured mercury speciation from OHM and SCEM differs greatly in the dense particle concentration flue gas. In particle-laden flue gas, the OHM can distinguish the particulate mercury speciation but the SCEM can better distinguish the gaseous mercury speciation. In the cleaned or ash-free flue gas, both OHM and SCEM provide consistent mercury speciations.

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煤粉炉烟气中汞浓度测试和分布

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摘要: 参照美国标准实验方法 (ASTM) 中关于汞的 OHM 等速取样和化学分析法, 结合汞的 SCEM 在线测量技术, 利用一多功能流动实验室, 对一满负荷运行的 100 MW 煤粉锅炉尾部烟气系统进行了单质汞、氧化态汞和颗粒态汞的现场测试和分析。得到了空气预热器、静电除尘器前后烟气中气态、固态和烟气中总汞的浓度及其分布。结果表明烟气中气态总汞的浓度随温度的降低发生着氧化态汞向颗粒态汞的转化。在 ESP 之后的清洁烟气中, OHM 和 SCEM 方法的测试结果吻合较好; 在含颗粒浓度较高的烟气中, 2 种方法存在较大的偏差, 原因在于 OHM 取样过滤器中形成一定厚度的飞灰。该飞灰颗粒对烟气中气态汞有吸附作用并形成颗粒汞。

关键词: 燃煤烟气; 汞形态; 在线测量; 安大略法 (OHM); 连续排放物监测 (SCEM)

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