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Migration and emission of mercury from circulating fluidized bed boilers co-firing petroleum coke and coal

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Abstract: The migration and emission of mercury (Hg) were studied for three 410t/h circulating fluidized bed (CFB) boilers co-firing petroleum coke and coal. Both the Ontario Hydro Method (OHM) and EPA Method 30B were employed to sample gas phase emissions of mercury from the flue gas, and to compare the agreement for different measurement methods in industrial application. Concurrent with flue gas sampling, solid and liquid samples like fuel, bottom ash, fly ash and gypsum, waste water, etc. were also collected to determine the total mass balance and map the mercury migration and emission from the power plant. The results showed that the mass balance rates ranged from 83.92%-122.68%, which can be considered to be acceptable and reliable. The vast majority of mercury emitted was distributed into fly ash and stack gas, accounting for 61.36%-67.71% and 22.22%-33.35%, respectively. The total Hg concentration measured by OHM is comparable with that by EPA Method 30B, while EPA Method 30B shows large advantages over the flexibility. The total Hg removal efficiencies of electrostatic precipitator (ESP)+wet flue gas desulfurization (WFGD) and fabric filter (FF)+WFGD are 81.8% and 73.4%-76.4%, respectively. The FF has better Hg^0 and Hg^{2+} removal efficiencies than the ESP. The landfilling of bottom ash, fly ash and gypsum appears likely to have little environmental effect on soil and the main emphasize should be focussedd on the wastewater treatment. The mercury emission factors in this study are in the range of 0.69 g/TJ-0.80 g/TJ. The CFB boilers equipped with ESP/FF +WFGD appears to have the potential to significantly reduce the Hg emission to atmosphere.
Keywords: Hg; circulating fluidized bed; co-firing of petroleum coke and coal; migration; emission.

Introduction

Mercury (Hg) and its compounds from anthropogenic sources has raised public environmental concerns because of its potential to cause persistent damage, biological accumulation and because of its extensive mobility(Zhou et al., 2015). Presently, Coal-fired power plants are considered to be the main anthropogenic source for Hg emissions into the atmosphere (Pacyna et al., 2010; Wang et al., 2013). It was reported that in 2010, about 24% of total global anthropogenic mercury emission were emitted from coal-fired power plants (AMAP/UNEP, 2013). To cope with the serious Hg pollution, the “Minamata Convention,” an international, legally-binding treaty to prevent Hg emissions and release was signed by 86 countries including China on October 2013 (Pudasainee et al., 2016). The Chinese government also established the latest emission standard of air pollutants for thermal power

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plants (GB 13223-2011 (National Standard of P.R. China), 2011), which requires emission values of Hg be limited to 30 μg/m^3.

The Hg in the flue gas mainly occurs in three forms: gaseous elemental mercury (Hg^0), gaseous oxidized mercury (Hg^{2+}) and particulate bound mercury (Hg^p). Of these forms, Hg^p can be effectively removed by particulate matter (PM) control devices such as electrostatic precipitator (ESP) and fabric filter (FF). Hg^{2+} can be easily captured by wet flue gas desulfurization system (WFGD) due to its high water solubility. In contrast, Hg^0 is the most stable species and its residence time is estimated to be several months to one year in the atmosphere (Fu et al., 2012; Wu et al., 2010). Moreover, Hg^0 cannot easily be removed by existing air pollution control devices (APCDs) because of its low water solubility and high volatility (Gao et al., 2013; Pavlish et al., 2003; Tan et al., 2004). Therefore, in order to meet the increasingly stringent mercury emission limits, it is necessary to analyze the distribution of Hg speciation in the flue gas from practical combustion systems.

In terms of measurement, there are mainly three methods for onsite mercury measurement: the Mercury Continuous Emission Monitoring System (Hg-CEMS), a wet chemistry based on the Ontario Hydro Method (OHM) and the sorbent trap method based EPA Method 30B. The Hg-CEMS is mainly used for monitoring real-time Hg emission from the stack(US EPA, 2010). The OHM is considered to be the standard and reference mercury speciation measurement method in flue gas employs this method but its complexity in operation and the potential for errors in solution preparation and analysis are non-negligible(Laudal, 1999). Recently, the EPA Method 30B which uses chemical-treated activated carbon (AC) as the sorbent has begun to be gradually accepted worldwide. It is seen as an effective alternative to OHM because of its convenient operation, high precision and low cost(Cheng et al., 2009a). However, the high price of imported sorbent traps and AC remains a problem for its wide industrial application in China.

Recently, the majority of Chinese power plants have been equipped with advanced APCDs, such as selective catalytic reduction (SCR)/selective non-catalytic reduction (SNCR), ESP/FF, WFGD with an aim to reduce the emission of nitrogen oxides (NO_x), particulate matter (PM) and sulfur dioxide (SO_2), respectively. However, the increase in the application of these APCDs not only increases the production of coal combustion byproducts (e.g., gypsum and WFGD wastewater), but also affect the partitioning behavior and emission of mercury. The concentration of Hg^{2+} in the flue gas increased and the Hg^0 concentration decreased after ESP (Lu et al., 2007) and chlorine in coal and unburned carbon in ash appears to be the primary component responsible for enhancement of mercury oxidation and capture in practical systems (Gale et al., 2008). The abatement capacity of WFGD for Hg ranges from 30.4%-78.4% and most of the Hg removed by WFGD was found in the WFGD gypsum (ÁLvarez-Ayuso et al., 2006; Cheng et al., 2009b; Meij et al., 2002). However, there is concern that disposal (e.g., landfill and deposit outdoor) and utilization of fly ash and gypsum (e.g., production of concrete) may have harmful impacts on environment and human health. Thus, the understanding of partitioning and redistribution behavior and of Hg across APCDs will help us to develop promising Hg emission control technologies in power plant.

Petroleum coke is a solid byproduct derived from petroleum refining process (Gross et al., 2003). As an alternative energy to traditional fossil fuel, the production of petroleum coke has been increasing with the rapid development of heavy oil processing. Petroleum coke

possesses high fixed carbon, high sulfur and low volatiles content, so it has serious potential pollutant emission like SO_2 and NO_x when burning it (Jia et al., 2002; Wang et al., 2004). Due to its high combustion efficiency, low pollutant emission and excellent fuel flexibility, circulating fluidized bed (CFB) technology appears to be an effective way to burn petroleum coke (Belin, 2002; Chen and Lu, 2007; Duan et al., 2008). Previous studies have mainly focused on mercury migration and emission in CFB boilers when burning fuels like coal, sewage, biomass, coal gangue and etc., and there is little research on mercury emission from burning mixed fuel of petroleum coke and coal (Åmand and Leckner, 2004; Li et al., 2012; Van de Velden et al., 2008; Zhang et al., 2015). In order to ensure the clean and effective use of petroleum coke, it is essential to study the migration and emission of mercury in CFB boilers co-firing petroleum coke and coal.

In this paper, field tests on mercury migration and emission characteristics were carried out at three 410t/h CFB boilers burning mixed fuel of petroleum coke and coal. The Hg concentration and speciation distribution was simultaneous sampled at the both inlet and outlet of ESP/FF, WFGD. The main objectives of this study are as follow: (1) mercury mass balance and its distribution; (2) determination of mercury concentration and speciation across APCDs based on both OHM and EPA Method 30B; (3) determination of mercury removal rate from APCDs; (4)the measurement of mercury contamination to the environment and emission factor.

2. Material and Methods

2.1 Utility boilers description

The migration and emission of Hg were studies at three CFB utility boilers. The detailed configurations of these units are shown in Table 1. The boilers rated capacities are 410 t/h. All tested boilers are installed with SNCR, ESP/FF and WFGD in series as APCDs to control the emission of NO_x, particulate matter and SO_2. The SNCR use urea as its denitrification reagent. The WFGD is a typical vertical spray tower based on limestone-gypsum, which consists of circulating pump, spray nozzles, spray layer, oxidation zone and demister.

Table 1

Configuration of tested boilers

Item	Boiler type	Capacity/($t \cdot h^{-1}$)	APCDs
#1	CFB	410	SNCR+ESP+WFGD
#2	CFB	410	SNCR+FF+WFGD
#3	CFB	410	SNCR+FF+WFGD

Of these units, boilers #1 burns 100% coal, both boiler #2 and boiler #3 burn mixed fuel of petroleum coke and coal with a blending ratio of 1:2. The proximate and elemental analysis of the fuels are shown in Table 2. According to the National Coal Classification Standard of China (GB/T 7562-2010), the mixed fuel sample can be classified as a bituminous coal when co-firing petroleum coke. Here, the fixed carbon and sulfur content in mixed fuel sample (boiler #2, boiler #3) are higher than those in coal sample (boiler #1), while the ash content in mixed fuel sample is lower than that in coal sample. The mercury content in coal and mixed fuel are 0.084 mg/kg and 0.066 mg/kg, respectively. Chlorine in coal is considered to be an important factor influencing mercury partitioning behavior. In this study, the chlorine content in coal and mixed fuel are 110 mg/kg and 77 mg/kg, respectively, which is significantly lower

than most of the coals used commercially in China (260mg/kg) and the United States of American (614mg/kg)(Zhang et al., 2012).

Table 2

Proximate and elemental analysis of tested fuels

Item	Proximate analysis				$Q_{ar,net}$	Elemental analysis						
	M_{ar}	A_{ar}	V_{ar}	FC_{ar}		C_{ar}	H_{ar}	O_{ar}	N_{ar}	S_{ar}	Cl	Hg
	%	%	%	%	MJ/kg	%	%	%	%	%	mg/kg	mg/kg
#1	11.18	16.80	22.40	49.62.	23.40	59.39	3.55	6.59	1.38	1.11	110	0.084
#2	10.14	11.41	18.07	60.38	26.15	66.48	3.48	4.99	1.37	2.12	77	0.066
#3	10.14	11.41	18.07	60.38	26.15	66.48	3.48	4.99	1.37	2.12	77	0.066

2.2 Sampling process

During the field test, the total mercury concentration in the flue gas was sampled based on the Ontario Hydro Method (OHM) and EPA Method 30B, respectively. The mercury speciation in the flue gas was analyze by OHM. Both sampling methods were tested simultaneously at three points, namely both the inlets and outlets of ESP/FF and WFGD. Detailed sampling locations of configuration of power plant were shown in Fig. 1.

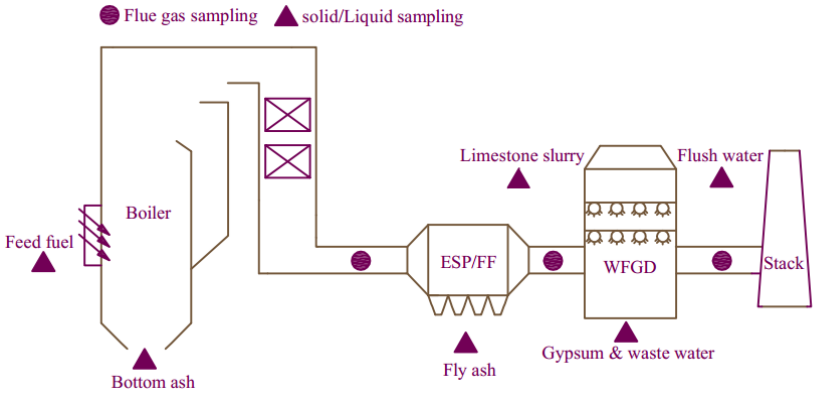


Fig.1. Schematic of sampling points across APCDs

The sampling equipment for two sampling methods was by means of an Apex mercury instrument made in USA. The flue gas sample was firstly extracted from gas duct isokinetically by a probe with a quartz fiber filter maintained at 120 ^{o}C to prevent the condensation of water vapor and the absorption of Hg vapor to the inner face of filter. The Hg^{p} was collected on a quartz fiber filter. Then for the OH method, the flue gas sample subsequently flows through a series of impingers placed in an ice bath. The Hg^{2+} was collected by the first three impingers containing 1mol/dm^3 KCl solution, and Hg^{0} was collected in the fourth impingers containing 5% V/V H_2O_2-10% V/V HNO_3 solution and the three impingers with a solution of 4% W/V $KMnO_4$-10% V/V H_2SO_4. The eighth impinger containing silica gel, which was used to remove the moisture from the previous impingers train before enter the following auxiliary equipment such as thermometer, vacuum gauge, air-tight pump, gas metering console and etc.

For EPA Method 30B, the flue gas sample after filtration will subsequently flow through the paired traps filled with potassium iodide-treated activated carbon (AC-KI) to capture the gaseous mercury. The AC-KI sorbents trap was derived from US Ohio Lumex Inc, which is made of Pyrex (heat-resistance glass) to prevent the condensation Hg vapor on the inner face.

Each trap consisted of two sorbent sections, the front section is for Hg collection and the rear section is there to allow for Hg break through. Each section contains 0.5 g sorbents and were separated by mercury-free fiberglass. Then the flue gas was dried before entering the following auxiliary equipment similarly to those used by OHM. The total gaseous Hg was calculated using the following equation:

$$C_{Hg} = \frac{m_1 + m_2}{V_t} \quad (1)$$

Where C_{Hg} is the total gaseous Hg, μg/Nm^3; m_1 and m_2 are the mass of Hg in the Hg collection section and Hg break through section, respectively, μg; and V_t is the total volume of dry gas measured during the sampling process, m^3.

The whole sampling process lasted for 2 h measured by OHM and 1h measured by EPA Method 30B, respectively. All sampling tests were conducted in twice to obtain duplicate results. The boiler conditions were kept stable during the field test. The schematic of the OHM and EPA method 30B sampling devices are shown in Figure 2 and Figure 3.

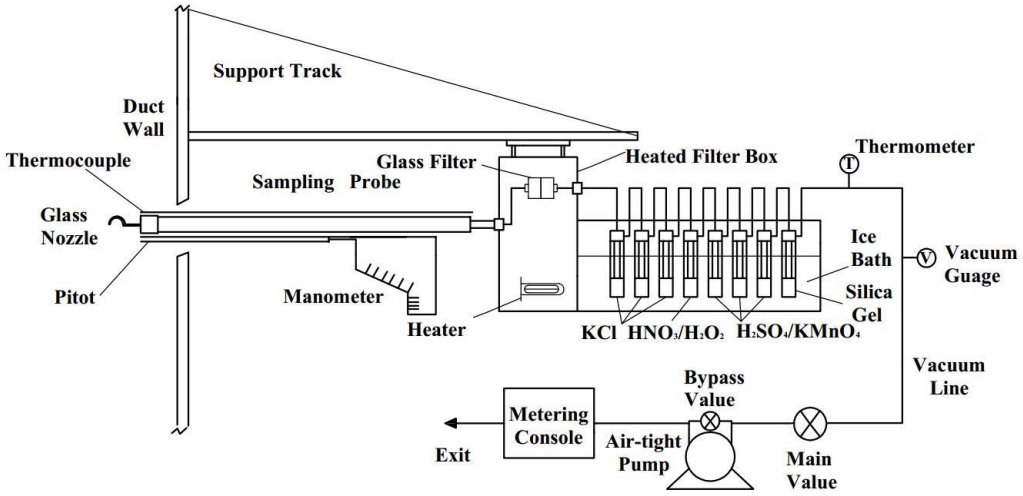


Fig.2. Schematic of the OHM sampling device

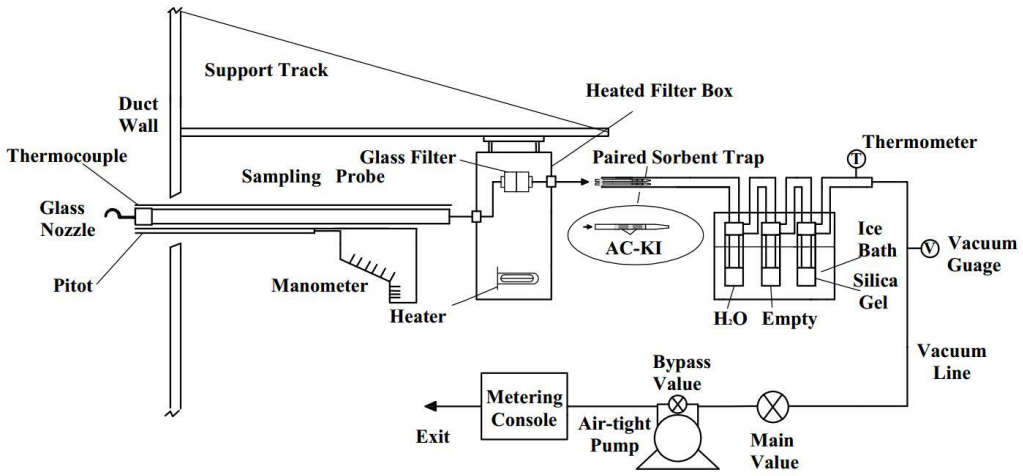


Fig.3. Schematic of EPA Method 30B sampling device

Concurrent with flue gas sampling, samples of feed fuel, bottom ash, ESP/FF ash,

limestone slurry, flush water, gypsum and WFGD wastewater were also collected every 0.5 h. Then the solid samples were preserved in self-sealed bag and the liquid samples were store in high boron silicon bottle for waiting lab Hg analysis.

2.3 Elementary analysis

The gaseous mercury including Hg^0 and Hg^{2+} in the absorbed solution was analyzed by the U.S. Leeman Hydra AA cold vapor atomic absorption spectrometer (CVAAS) after recovery and digestion, which is based on the ASTM D22.03.01. Solid samples like sorbents in traps, feed fuel, bottom ash, ESP/FF ash and gypsum were initially air-dried to constant weight, and then milled and pulverized to below 200 mesh. The mercury in pulverized samples was determined by Milestone DMA-80 Direct Mercury Analyzer, which is based on the ASTM D6722-01. Mercury in liquid samples like limestone slurry and wastewater was determined by atomic fluorescence spectrometry (AFS) based on HJ694-2014, which is a national standard for China. All mercury analysis was carried out at least twice to produce duplicate results and reduce experimental uncertainties.

3. Results and Discussion

3.1 Mercury mass balance and distribution

The mass balance rate was calculated as the output in all forms of combustion byproducts including bottom ash, fly ash, gypsum, WFGD wastewater and flue gas to the input from feed fuel, flush water and limestone slurry. The Hg mass balance rates at three

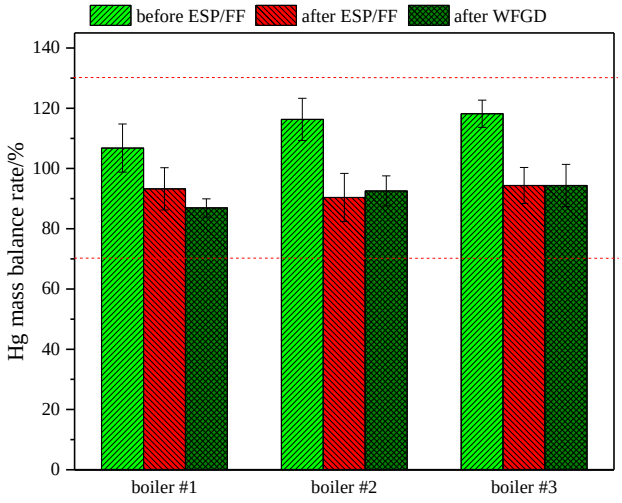
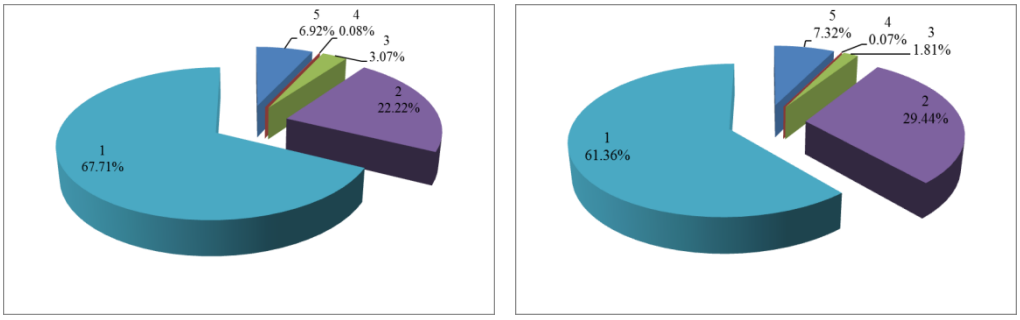


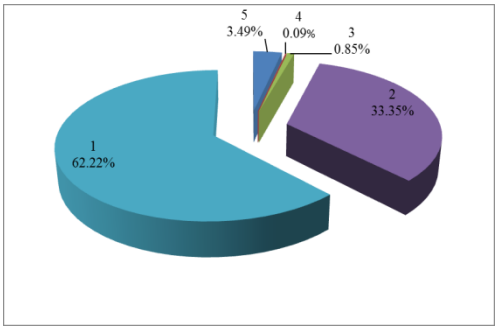
Fig.4. Hg mass balance rate at three sampling locations

sampling locations are shown in Fig. 4. Due to the fluctuation of boiler operating conditions and the uncertainties in sampling and analysis procedure, it is acceptable for these values to be in the range of 70%-130%(Wang et al., 2009). For all of the tested boilers, the mass balance rates ranged from 83.92%-122.68%, which confirms reliability and validity of mercury field test data in power plant.

Base on the mercury mass balance ratio, the mercury distribution in all forms of combustion byproducts for the whole system was shown in Fig.5. As shown in Fig.5, the vast



(a) (b)



(c)

Fig.5. mercury distribution in all forms of combustion byproducts for the whole system (a) boiler #1 (b) boiler #2 (3) boiler #3

(1 fly ash, 2 stack gas, 3 WFGD wastewater, 4 bottom ash, 5 WFGD gypsum)

bulk of the mercury output was distributed into the fly ash and stack gas, accounting for 61.36%-67.71% and 22.22%-33.35%, respectively. The proportion of mercury in bottom ash is extremely low, only accounting for only 0.07%-0.09% of the total Hg emissions. This is due to the fact that given the high temperature in furnace, most of the Hg in the coal will be vaporized and released to flue gas, and as a result, only a tiny fraction of the mercury remains in the bottom ash. When the flues gas flow through WFGD, about 3.49%-7.32% of Hg was removed by gypsum, and 0.85%-3.07% of Hg was removed by WFGD wastewater, respectively. This arises because the dissolved Hg^{2+} in the slurry can react with sulfide or sulfur oxides in the flue gas to form insoluble mercury sulfide or sulfate. A portion of mercury sulfide or sulfate can be absorbed by the gypsum, while the rest will remain in the wastewater because of the vacuum dewatering effect.

3.2 Mercury concentration and speciation across APCDs

The total mercury concentration across APCDs measured by OHM and EPA Method 30B is shown in Table 3. It can be seen from the Table 3 that at the outlet of boilers and WFGD, the mercury concentration in the flue gas was in the range of 9.58-12.07 μg/m^3 and 2.20-2.84 μg/m^3, respectively. The Hg concentration in the flue gas at both sampling locations is far lower than the mercury limit value of 30 μg/m^3 specified by GB 13223-2011. By comparison for these two sampling methods, the relative deviation between the OHM and EPA Method 30B was in

Table 3

Hg concentration across APCDs of CFB power plant measured by OH Method and EPA Method 30B (on the basis of standard dry flue gas, 6% O_2 normalized)

Item	Sampling method	Inlet of ESP/FF	Outlet of ESP/FF	Outlet of WFGD

		μg/Nm^3	μg/Nm^3	μg/Nm^3
	OHM	12.07	3.82	2.20
#1	EPA Method 30B	11.71	4.19	2.34
	RD[a] (%)	3.1	8.8	6.0
	OHM	9.58	2.72	2.26
#2	EPA Method 30B	10.07	2.86	2.47
	RD[a] (%)	4.9	4.9	8.5
	OHM	9.85	2.96	2.62
#3	EPA Method 30B	9.73	3.23	2.84
	RD[a] (%)	1.2	8.4	7.7

[a]RD: relative deviation of the total mercury concentration measured by OHM and EPA Method 30B.

the range of 1.2%-8.8%. Due to the fluctuation of boilers parameters and differences of sampling and analysis methods, some relative deviation between these two methods is inevitable and but given their low levels the RD can be considered acceptable. Thus, the total Hg concentration measured by OHM is quite comparable with that by EPA 30B. Moreover, because of its simple operation, high precision and rigorous quality assurance procedures, EPA Method 30B can currently be considered to be the most likely alternative to the cumbersome OHM method(Laudal, 2009).

The concentration and proportion of mercury speciation in the flue gas across each APCD are shown in Table 4. These APCDs are installed to remove NO_x, PM and SO_2, but will also have a co-beneficial effect on Hg capture. It can be seen from Table 4 that Hg^p is the main Hg form at the inlet of ESP/FF namely the outlet of the boilers, with proportional values ranging from 48.02%-59.82%. Several studies found that the proportion of Hg^p in the flue gas from CFB boilers is generally higher than that from pulverized-coal (PC) boilers. This can be explained by the fact that the CFB boilers generally has a higher unburned carbon (UBC) content in fly ash, and withmore sufficient contact between gaseous mercury and fly ash, this will enhance the absorption of Hg on fly ash (Yin et al., 2013; L. Zhang et al., 2016; Y. Zhang et al., 2016). In addition, the proportion of Hg^p at the outlet of boiler #1 (59.82%) is higher than that seen at the outlet of boiler #2 and boiler #3 (ranged from 48.02%~49.69%), which is consistent with the higher mercury and chlorine content in the coal of boiler #1 (as shown in Table 2).

Table 4

Mercury speciation and concentration across each APCD of CFB power plant (on the basis of standard dry flue gas, 6% O_2 normalized)

Item	Hg speciation	Inlet of ESP/FF		Outlet of ESP/FF		Outlet of WFGD	
		μg/Nm^3	%	μg/Nm^3	%	μg/Nm^3	%

#1	Hg^0	3.55	29.41	2.45	64.14	2.01	91.36
	Hg^{2+}	1.30	10.77	0.83	21.73	0.10	4.55
	Hg^p	7.22	59.82	0.54	14.14	0.09	4.09
	Hg^T	12.07	100	3.82	100	2.05	100
#2	Hg^0	3.33	34.76	2.17	79.70	2.22	98.23
	Hg^{2+}	1.49	15.55	0.51	18.73	0.04	1.77
	Hg^p	4.76	49.69	0.04	1.57	0.00	0.00
	Hg^T	9.58	100	2.72	100	2.26	100
#3	Hg^0	4.03	40.91	2.50	84.51	2.58	98.47
	Hg^{2+}	1.09	11.07	0.41	13.86	0.04	1.53
	Hg^p	4.73	48.02	0.05	1.63	0.00	0.00
	Hg^T	9.85	100	2.86	100	2.49	100

3.2.1 ESP/FF

ESP/FF are widely utilized in power plants in China to remove the PM from the flu gas. Unlike ESP, where performance may vary significantly depending on electrical conditions and physical property of particle (e.g. particle size and dust specific resistance), the FF system has the capacity to remove submicron particles with the removal efficiency of 99% (Wang et al., 2008; Zhang et al., 2008). As shown in Table 4, the proportion of Hg^p reduced from 48.02%-59.82% to 1.57%-14.14% after through ESP/FF, indicates that most of Hg^p can be removed by ESP/FF along with particulate matter removal. Compared with gaseous Hg^0, the concentration of gaseous Hg^{2+} decreased more sharply when flue gas passes through ESP/FF. Because of their differences in property and reactivity, gaseous Hg^{2+} can be absorbed on the fly ash more effectively and thus would be expected to be removed by ESP/FF (Srivastava et al., 2006; Y. Zhang et al., 2016). In addition, the total gaseous mercury (including Hg^0 an Hg^{2+}) concentration decreased 32% and 44% on average when flue gas pass through ESP and FF unit, respectively, indicating that the FF has better Hg^0 and Hg^{2+} removal efficiencies than the ESP. Previous studies found that the filter dust cake layer can facilitate the oxidation of Hg^0, and ensure more contact between gaseous mercury and fly ash occurred when flue gas flows through filter medium inside the FF system (Gao et al., 2013; Wang et al., 2016).

3.2.2 WFGD

The WFGD is used in power plant for SO_2 control, and uses a lime or limestone slurry as reagent to react with the SO_2. As shown in Table 4, the Hg^{2+} concentration decreased sharply across the WFGD, with the proportion of Hg^{2+} ranging from 13.86%-21.73% to 1.53%-4.55%. This is due to the fact that Hg^{2+} is highly water-soluble and can react with dissolved sulfides (e.g. H_2S) in the flue gas to form insoluble mercury sulfide, which are ultimately removed by WFGD (Liu et al., 2013; Rallo et al., 2010). This could be interrupted by reactions (2) and (3).

$$H_2S \rightarrow H^+ + HS^- \quad (2)$$

$$Hg^{2+} + HS^- \rightarrow HgS\downarrow + H^+ \quad (3)$$

In addition, the concentration of Hg^p decreased by 83%-100%, which indicates the Hg^p can be captured by WFGD effectively. Interestingly, the Hg^0 concentration deceased when flue gas pass through WFGD at boiler #1, while it increased slightly at boiler #2 and boiler #3. The decrease of Hg^0 concentration, can be explained as due to part of Hg^0 being oxidized to Hg^{2+}. For the increase of Hg^0 concentration, the reasons are more complex, but can be

explained as following (Córdoba et al., 2011; Ochoa González et al., 2012): here, the Hg^{2+} and Hg^0 in the flue gas can react to form Hg_2^{2+}, and subsequently the Hg_2^{2+} will react with active OH^- in the slurry to form Hg^0 and HgO. The HgO can further be reduced by SO_2 in the flue gas to form Hg^0. The above process can be represented by reactions (4)-(6). The other factor, is that there is sulfite or sulfate generated from the reaction between SO_2 in the flue gas and aqueous slurry. These species can react with dissolved Hg^{2+} in the slurry to form mercury sulfite ($HgSO_3$) and mercury sulfate ($HgSO_4$), both of which are unstable. In this case, a portion of mercury sulfite and mercury sulfate decomposes into Hg^0 via reactions (7) and (8):

$Hg^{2+} + Hg^0 \rightarrow Hg_2^{2+}$ (4)

$Hg_2^{2+} + 2OH^- \rightarrow H_2O + HgO + Hg^0$ (5)

$HgO + SO_2 \rightarrow Hg^0 + SO_3$ (6)

$Hg^{2+} + SO_3^{2-} \rightarrow HgSO_3 \rightarrow Hg^0$ (7)

$Hg^{2+} + SO_4^{2-} \rightarrow HgSO_4 \rightarrow Hg^0$ (8)

In general, the re-volatilization of Hg^0 is influenced by multiple factors such as flue gas and slurry composition, slurry pH, flue gas temperature and limestone injection rate (Ancora et al., 2015; Ochoa González et al., 2012; Schuetze et al., 2012). A previous study (Chang and Ghorishi, 2003) found that when the pH of slurry decreased, according to reaction (9) and (6), the SO_2 concentration in the gas phase will increase, which will enhances the reemission of Hg^0. (Zhang et al., 2016) compared the flue gas temperature at the inlet of WFGD in two power plants and found that the increase of flue gas temperature in the scrubber might also result in the increase of Hg^0 reemission.

$H_2O + SO_2 \rightleftarrows H_2SO_3 \rightleftarrows H^+ + HSO_3^- \rightleftarrows 2H^+ + SO_3^{2-}$ (9)

3.3 Mercury removal efficiency of APCDs

The Hg removal efficiencies across each APCDs and the entire system are summarized in Fig.6. As shown in Fig.6, the total Hg removal efficiencies across ESP and FF are 68.3% and 70.0%-71.6%, respectively. These results are similar to values measured in Chinese and American plants with value of 62.2%-76.4% for ESP and 67%-91% for FF (Pavlish et al., 2003; Pudasainee et al., 2016; Yueyang et al., 2014). The total Hg removal efficiencies across WFGD from boiler #2 and boiler #3 (ranged from 11.32%-16.92%) are lower than that from boiler #1 (42.41%), and this can be attributed to the reemission of Hg^0 and the relative lower proportion of Hg^{2+} presented at the inlet of WFGD from boiler #2 and boiler #3. Previous studies (Senior, 2007; Tang et al., 2016) found that the use of high-chlorine coal, SCR and halogen addition can increase the Hg^{2+} proportion in flue gas before WFGD, which will enhance the overall mercury removal efficiency of WFGD. The total Hg removal efficiencies of ESP+WFGD and FF+WFGD are 81.8% and 73.4%-76.4%, respectively, which indicates that CFB+ESP/FF+WFGD have a remarkable co-beneficial effect on mercury capture.

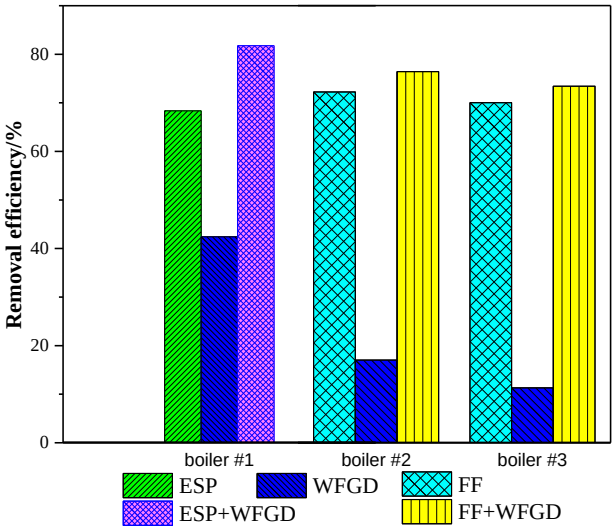


Fig.6. Hg removal efficiencies of APCDs

3.4 Environmental implication

3.4.1 Hg contamination on environment

The application of APCDs can significantly increase the production of combustion byproducts (e.g. bottom ash, fly ash, WFGD wastewater and gypsum). During coal combustion process, a large portion of Hg can be removed by APCDs and then be transformed into solid and liquid combustion byproducts. As a result, the disposition of combustion byproducts (e.g. landfilling) and reutilization (e.g. construction) should be paid more attention. Table 5 presents the Hg concentration in combustion byproducts and limit values for soil and surface water proposed by the State Technical Supervision Bureau and National Environmental Protection Agency of China (GB 15618-1995 (National Standard of P.R. China), 1995; GB 3838-2002 (National Standard of P.R. China), 2002). For the solid combustion byproducts, the Hg concentrations, are below limit value specified by GB15618-1995, indicating that the landfilling of bottom ash, fly ash and gypsum will have little environmental effect on soil. However, the reutilization of fly ash and gypsum in applications such as cement and wall board production respectively, can cause Hg reemission into atmosphere during any calcining process (Liu et al., 2013; Rallo et al., 2010). For liquid combustion byproducts, the Hg concentration in the WFGD wastewater significantly exceeds the limit value, which indicates that great emphasizes should be put on the wastewater treatment.

Table 5

Hg concentration in combustion byproducts (on the wet basis)

Item	#1	#2	#3	Limit value
Bottom ash (μg/kg)	1.76±0.14	1.94±0.17	2.37±0.21	500[a]
Fly ash (μg/kg)	375.81±9.87	389.76±10.25	401.35±13.64	500[a]
Gypsum (μg/kg)	50.15±4.23	34.92±2.76	22.34±1.58	500[a]
Wastewater (μg/L)	25.68±1.25	10.05±0.56	6.27±0.27	0.1[b]

[a] Environmental quality standard for soils (secondary level standard), GB15618-1995

[b] Environmental quality standard for surface water (third level standard), GB3838-2002

3.4.2 Atmospheric mercury emission factor

A mercury emission factor (MEF) is a significant parameter that evaluates the intensity of Hg emission into the atmosphere from power plant. In this study, the MEF is expressed as follow:

$$MEF=\frac{M_S}{F\times LHV} \qquad (10)$$

Where MEF is Hg mercury emission factor, g/TJ; M_s is the amount of Hg released to the air, t/h; LHV is the lower heating value of fuel, MJ/kg. The MEF of three tested boilers are 0.69 g/TJ for boiler #1, 0.70 g/TJ for boiler #2 and 0.80 g/TJ for boiler #3, respectively. The US EPA has determined the MEF of 80 power plants burning different type of coals (U.S. Environmental Protection Agency, 2004). The average emission factors of these power plants burned bituminous, subbituminous and lignite were 1.63 g/TJ, 2.08 g/TJ and 6.79 g/TJ, respectively. In a previous study (Zhang et al., 2016) reported the MEF of Chinese power plants with ultra-low emission APCDs was in the range of 0.39g/TJ-0.81g/TJ. It can be concluded that the emission factors obtained in this study are significantly lower than the values of US plants, but are close to the values of Chinese ultra-low emission power plants, which indicates that CFB boilers equipped with ESP/FF +WFGD have the potential to significantly reduce the Hg emission to atmosphere. However, the MEF is affected by the variation of boiler type, fuel type, equipment of APCDs, components in the flue gas and etc. Therefore, more onsite investigations are needed to obtain a comprehensive understanding of Hg emission characteristics in CFB power plants.

4. Conclusions

Studies on migration and emission of Hg were carried out on three circulating fluidized bed boilers power plants co-firing petroleum coke and coal and the following results were obtained:

(1) The mass balance rates ranged from 83.92%-122.68%, which can be considered to be acceptable and reliable values. The vast majority of output mercury was distributed into fly ash and stack gas, accounting for 61.36%-67.71% and 22.22%-33.35%, respectively. Hg in bottom ash represents the smallest ratio with 0.07%-0.09%.

(2) The total Hg concentration in the flue gas measured by OH method was comparable with that measured by EPA method 30B. Particulate-bound Hg is the main from existing at the inlet of ESP/FF, with a values ranging from 48.02%-59.82%.

(3) The FF has better Hg^0 and Hg^{2+} removal efficiencies than the ESP system. Hg^{2+} can be captured by WFGD but Hg^0 reemission has a negative effect on the Hg removal by WFGD. Overall, the total Hg removal efficiencies of ESP+WFGD and FF+WFGD are 81.8% and 73.4%-76.4%, respectively.

(4) The landfilling of bottom ash, fly ash and gypsum is likely to have little environmental effect on soil and great emphasizes should be placed on the wastewater treatment. The mercury emission factors in this study are in the range of 0.69 g/TJ-0.80 g/TJ, which is significantly lower than the values seen for US plants.

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Migration and emission of mercury from circulating fluidized bed boilers co-firing petroleum coke and coal

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