

Characterization of Mercury Emissions from a Coal-Fired Power Plant

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Received April 14, 2006. Revised Manuscript Received August 29, 2006

An emissions study for mercury was conducted at a 300 MW coal-fired plant equipped with an electrostatic precipitator (ESP). The input and output streams such as coal, slag, ESP ash, and flue gas were collected. Gaseous mercury was sampled using the Ontario Hydro method. The experimental data indicate that the majority of mercury goes into flue gas. The mercury quantity in flue gas to total combustion products is about 83%. The distribution of mercury in slag and fly ash is about 1 and 13%, respectively. The result also shows that, among the stack emissions after ESP, the gaseous mercury concentration in the flue gas is about 13–21 $\mu\text{g N}^{-1} \text{m}^{-3}$. The proportion in particulate form was extremely low; the content of Hg^{2+} in flue gas is about 55–69%; and the content of Hg^0 is about 31–45%. In addition, the absorption mechanism of mercury in fly ash was studied. It was found that the mercury concentration in fly ash is independent of the particle size and has a positive correlation with the loss of ignition of fly ash.

1. Introduction

Mercury is a leading concern among the air-toxic metals addressed in the 1990 Clean Air Act Amendments (CAAA) because of its volatility, persistence, and bioaccumulation in the environment and its neurological health impacts. Coal-fired utility boilers are now identified as the major source of mercury.^{1–3} March 15, 2005, the U.S. Environmental Protection Agency (EPA) issued the Clean Air Mercury Rule to permanently cap and reduce mercury emissions from coal-fired power plants.⁴ Although mercury is present in low ($\mu\text{g/g}$) concentrations in coal, the geometric mean of 0.22 $\mu\text{g/g}$ with a large volume of coal consumed makes coal-fired utility boilers one of the largest sources of mercury, releasing approximately 214 tons of mercury into the atmosphere in 1995 in China.⁵

Mercury in coal occurs in association with pyrite and other sulfide minerals and may also be organically bound.³ Coal mercury is converted to gaseous Hg^0 in the combustion flame and subsequently partially oxidized as the combustion gases cool. Mercury oxidation in boiler systems is kinetically controlled; homogeneous oxidation reactions are promoted by chlorine and atomic chlorine,⁶ and heterogeneous oxidation is

promoted by fly ash and sorbents.⁷ Oxidized mercury from coal combustion is generally thought to be HgCl_2 .⁸

To understand the fate of this element in modern coal combustion, investigations have been carried out and are now in progress in China. In this study, we investigated the characterization of mercury emissions in a 300 MW coal-fired plant equipped with electrostatic precipitators (ESPs). The objectives of this study were to (i) examine the Hg concentration in stack emissions, (ii) calculate overall mass balances and relative distribution of mercury in the power plant, and (iii) gain insight into the absorption mechanism of mercury in fly ash.

2. Experimental Section

2.1. Sampling. This study was carried out in a 300 MW pulverized coal-fired power station, which uses a tangentially fired boiler, WR direct flow burner manufactured by the CE Company. The power plant does not use staged combustion for NO_x control. Normal coal consumption is about 136 tons per hour during the full load operation of the power plant. During the course of the experiment, coal consumption was about 78 tons per hour at a 180 MW load. The fraction of coal particles larger than 88 μm is 11–15%. The same type of coal was burned for 5–6 days, including the presampling and sampling to provide a stable environment. The coal data are shown in Table 1. The ash produced by the boilers is about 12% slag and 88% fly ash.

Flue gas cleaning equipments are ESPs with an average removal efficiency of about 99.6%. Four electrically separated zones are installed in the direction of the flue gas flow. Each zone has its own hopper. Coal samples were a composite from samples taken at 15 min intervals during the flue gas sampling. Grab samples of slag were synchronized with hopper fly ash sampling. EF-1 is indicated for ash collected in hopper 1, and EF-2 is indicated for ash collected in hopper 2, etc. The ash carried away with the flue

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Table 1. Proximate and Ultimate Analyses of the Coal Sample

proximate analysis (wt %, as received)				ultimate analysis (wt %, daf)				
moisture	VM ^a	ash	FC ^a	C	H	N	S	O
0.28	12.97	29.75	56.00	57.30	3.68	0.74	1.97	6.59

^a VM, volatile matter; FC, fixed carbon.

Table 2. Concentration of Oxides and Coal and Fly Ashes (wt %)

	SiO ₂	Al ₂ O ₃	CaO	Fe ₂ O ₃	K ₂ O	MgO	Na ₂ O	TiO ₂
coal ash	54.92	26.15	8.64	6.44	1.08	0.82	0.08	1.07
EF-1	57.91	26.79	5.74	5.37	1.23	1.02	0.063	1.17
EF-2	51.56	31.03	8.42	5.84	1.24	0.99	0.076	1.33
EF-3	56.81	28.47	5.02	5.31	1.37	1.09	0.062	1.47
EF-4	58.52	26.01	5.87	5.39	1.12	0.78	0.063	1.44
PFA	59.31	25.70	4.17	5.27	1.77	1.46	0.058	1.39

gases out of ESPs will be termed particulate fly ash (PFA) in this paper. The flue gas streams were sampled downstream of ESPs using the Ontario Hydro method. Figure 1 shows the arrangement of the sampling system used. The flue gas is sampled isokinetically using a heated probe. Particulate matter was collected on a quartz fiber filter, and the vapor-phase samples were absorbed in an impinger train. Eight chilled impingers were connected in series with leak-free ground glass fittings. The first, second, and third impinger contains 100 mL of the 1 N KCl solution to catch oxidized mercury. The fourth impinger contains 100 mL of 5% HNO₃/10% H₂O₂, and the fifth, sixth, and seventh impinger contains 100 mL of 4% KMnO₄ (w/v)/10% H₂SO₄ (v/v) to absorb and retain elemental mercury in the gaseous phase. The last contains approximately 200–300 g of preweighed silica gel to determine the moisture gain and prevent moisture condensation in the pump and metering device. The flue gas temperature at this point is approximately 150 °C.

2.2. Analytical Methods. The concentration of major elements in coal and fly ash were determined by inductively coupled plasma-atomic emission spectrometry. The analyses of mercury in the coal, coal fly ash, and slag were performed by an atomic fluorescence spectrometer. The validity of the determination was ensured by triplicate analyses and standard addition methods. Certified reference material GBW08401 fly ash (Research Center for Eco-environmental Sciences, The Chinese Academy of Sciences) was also analyzed as an independent check.

Sample Recovery of PFA. At the end of a sampling period, the probe was cooled prior to sample recovery. The filter was removed carefully from the filter holder and placed in its labeled Petri dish container. Particulate matter and any condensate were recovered quantitatively from the probe nozzle, probe fitting, probe liner, and front half of the filter holder by washing these components with 0.1 N HNO₃ solution.

Sample Recovery of Mercury in Impingers. The impinger train sample recovery scheme is illustrated in Figure 2. Just before doing the analysis, 1 mL of 10% hydroxylamine solution was added to the sample until the sample became clear. All of the prepared solutions were analyzed by a cold-vapor atomic fluorescence spectrometer.

The particle-size distribution of the as-received ash was determined in the range of 0.05–900 μm using laser diffraction (MNM5004, Malvern, U.K.). Because of the low particulate loadings, it is difficult to sample enough PFA carried away with the flue gases out of ESPs for analysis; only hopper fly ashes were assessed.

3. Results and Discussion

3.1. Mercury Distribution in the Combustion Product. The concentration of oxides of coal and fly ash is shown in Table 2. The particle-size distribution analysis of the fly ash from four ESP fields is shown in Table 3 and Figure 3. The particle-size distribution of EF-1, EF-2, EF-3, and EF-4 is 0.31–140.58,

Table 3. Particle-Size Analysis of Fly Ash

sampling site	size				D(4,3) ^a (μm)
	10–30 μm (%)	<10 μm (%)	<2.5 μm (%)	<1.0 μm (%)	
EF-1	38.6	17.3	2.0	0.8	35.49
EF-2	33.8	58.7	12.6	4.0	11.97
EF-3	6.2	93.8	38.8	11.2	4.30
EF-4	3.2	96.9	41.7	11.7	3.84

^a D(4,3) represents the bulk particle size obtained using the volume average method.

Table 4. Mass Balance of Hg between Output and Input Streams in a Coal-Fired Power Plant

	stream	unit	result
input output	coal	g/h	25.58
	slag	g/h	0.12
	EP-1	g/h	1.75
	EP-2	g/h	0.47
	EP-3	g/h	0.11
	EP-4	g/h	0.06
	PFA	g/h	0.02
	flue gas after ESP	g/h	15.68
mass balance	(output/input)/100	%	71

0.09–56.23, 0.09–22.49, and 0.09–14.22 μm, respectively. When going from EF-1 to EF-4, the <10 μm size fraction (the “respirable” particles) increases from 17.26 to 96.85%, the <2.5 μm size fraction increases from 2.0 to 41.7%, and bulk particle size D(4,3) decreases from 35.49 to 3.84 μm. Therefore, when we go from hopper 1 to hopper 4, the particle size of fly ash decreased. It could also be considered that the particle size of the PFA is finer than that of ash collected in hopper 4 and smaller than 10 μm.

The term “relative enrichments” was introduced to properly describe the observed behavior.⁹ The relative enrichment factor (RE) is defined as

$$RE = \frac{(\text{element concentration in ash})}{(\text{element concentration in coal})} \frac{(\text{percent ash content in coal})}{100}$$

The concentration of mercury in coal, fly ashes, and the REs derived from them are shown in Figure 4. The RE factors are very small ($\ll 1$), no matter whether they are in slag, fly ash, and the smallest fly particles (PFAs), which means that, in the combustion zone of a coal-fired boiler, all of the mercury in the coal is vaporized as vapor-phase mercury. With the route of the flue gases through the boiler, air preheater, and the ESPs, the temperature decreases to 150 °C, with only a small proportion being retained on the ash particles.

Overall mass balances for mercury have been calculated assuming that only input is the mercury content of the combusted coal. Process outputs are hopper fly ash, slag, and in-stack mercury in the form of particulate and gas species. The quantities of the coal burnt during the tests are known and, from the proximate and ultimate analyses, the total volume of gas produced during the test has been calculated. The quantity of PFA collected on the filter and total volume of flue gas sampled are known from the sampling experiments. Through determination of mercury content in the absorbent solution, the mercury concentration of the flue gas is also determined. To manually determine the total amount of ash deposited in the four electric fields and slag throughout the experiment would be practically

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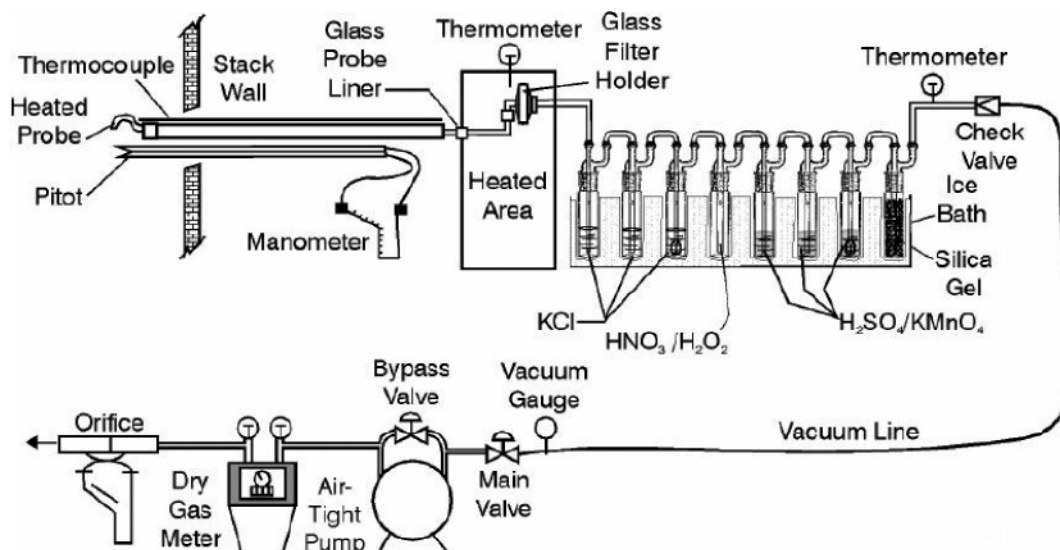


Figure 1. Arrangement of the Ontario Hydro method for stack sampling.

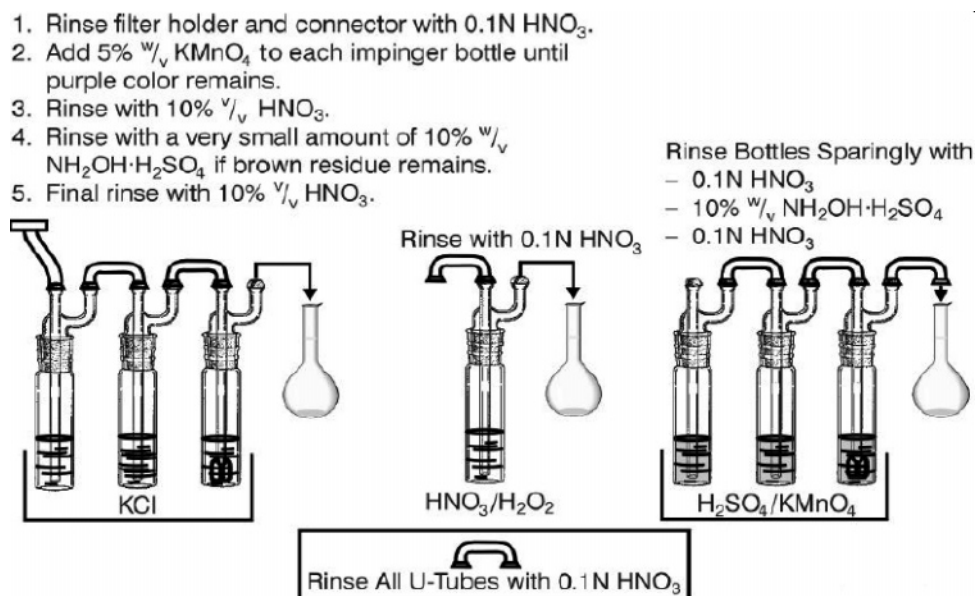


Figure 2. Sample recovery scheme for the mercury impinger train.

impossible. The quantities of fly ash and slag have been estimated mathematically using the assumption that the ash produced by the boilers is about 12% slag and 88% fly ash. The total mass efficiency of ESP is 99.6%, and each ESP row captures 75% of the ash entering that row (on the basis of annual figures of the power station). The mass efficiency from the first electric field to the fourth electric field account for total fly ash is 75, 18.75, 4.68, and 1.17%, respectively. The mass balance date is shown in Table 4.

The sampling and analytical techniques are very complex, and the results include some uncertainty. Uncertainty includes fluctuations in coal, flue gas flow rates, sampling, and measurement uncertainty. It is usually difficult to estimate each uncertainty separately. The recovery of mercury is 71%, within the accepted bound of 70–130%. Although the use of range values and standard deviations must be considered, we focused on the overall contributions of the flue gas cleaning system in the coal-fired plant to the stack emissions and the characteristics of the coal residues. As can be seen from Figure 5, the percentages of mercury in the slag, fly ash, and stack emissions are 1, 13, and 86%, respectively. This means that the high proportion of mercury would be emitted to the atmosphere after

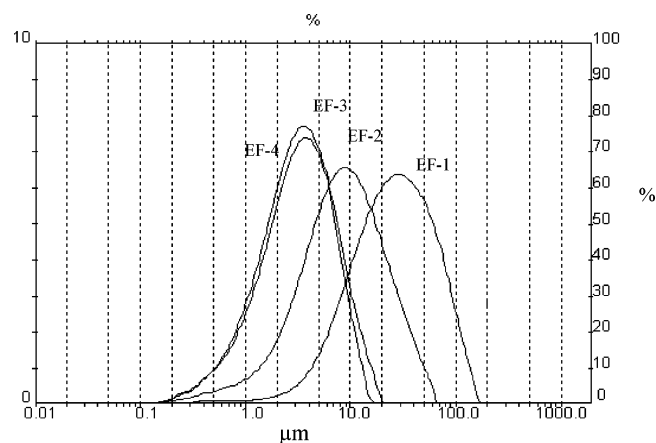


Figure 3. Size distribution of fly ash.

passing through the particulate controls, which is similar to that observed by other researchers.¹⁰ The experimental data show that the mercury concentration of flue gas is $21.15 \mu\text{g N}^{-1} \text{m}^{-3}$, which may increase the risk of pollution after emission to the atmosphere.

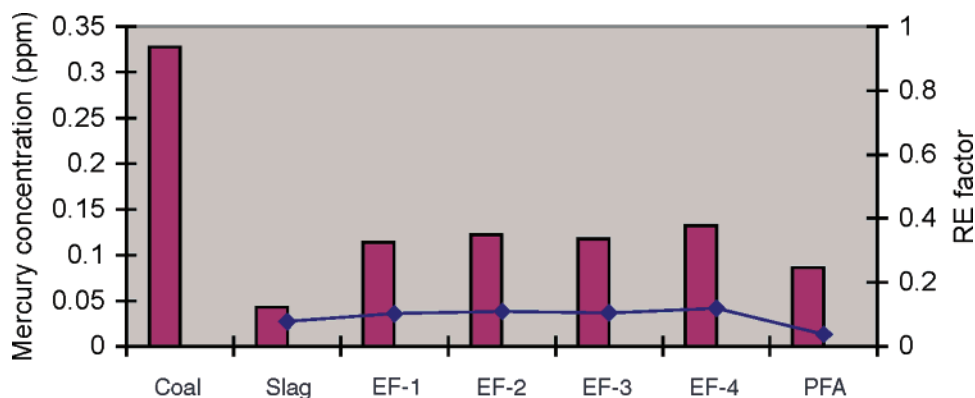


Figure 4. Contents of mercury in coal and its combustion products and the EF_s derived from them.

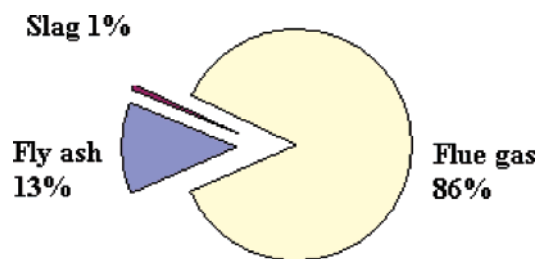


Figure 5. Quantitative distribution of mercury in combustion products.

3.2. Speciation of Mercury in Vapor-Phase Mercury. The term speciation is used to denote the relative amounts of these three forms of Hg in the flue gas of the boiler: (i) elemental Hg (represented by the symbol Hg⁰), (ii) compounds of oxidized Hg (represented by the symbol Hg²⁺), and (iii) particle-bound mercury. At present, speciation of Hg in the flue gas from a coal-fired electric utility is not well-understood. A number of laboratory and field studies have been conducted or are ongoing to improve the understanding of the transformation of Hg⁰ to the other Hg forms in the flue gas downstream of the boiler furnace. Data obtained to date indicate that combinations of many factors affect the speciation of Hg in the flue gas. These factors include the type and properties of the coal burned, combustion conditions in the boiler furnace, boiler flue gas temperature profile, boiler flue gas composition, boiler fly ash properties, and postcombustion flue gas cleaning technologies used.

The Ontario Hydro method applies to the determination of elemental, oxidized, particle-bound, and total mercury emissions from coal-fired stationary sources. Because of the low particulate loadings after ESPs, it is difficult to sample enough PFA without contamination to carry out element analysis during flue gas sampling time (60 min). The PFA has to be sampled separately for another relatively long time. In comparison to the content of oxidized mercury and elemental mercury, the particle-bound mercury could be ignored in the flue gas after ESPs. Sampling was conducted over a period of 3 days at the same conditions. Table 5 provides a summary of the gas-phase mercury sampling results for all of the tests.

The vapor phase emissions of mercury vary over the range 13.65–21.15 $\mu\text{g N}^{-1} \text{m}^{-3}$. A total of 31–45% of the mercury that was present in the stack gas was in the elemental form, and 55–69% of the mercury was in the oxidized form. When the coal is burned in an electric utility boiler, the resulting high combustion temperatures in the vicinity of 1500 °C vaporize

Table 5. Distribution of Hg⁰ and Hg²⁺ in Vapor-Phase Mercury

sample	Hg ²⁺		Hg ⁰		total mercury ($\mu\text{g N}^{-1} \text{m}^{-3}$)
	($\mu\text{g N}^{-1} \text{m}^{-3}$)	(%)	($\mu\text{g N}^{-1} \text{m}^{-3}$)	(%)	
1	8.508	55	6.962	45	15.47
2	14.593	69	6.557	31	21.15
3	8.599	63	5.051	37	13.65

the Hg in the coal to form gaseous elemental Hg⁰. Subsequent cooling of the combustion gases and interaction of the gaseous elemental Hg with other combustion products result in a portion of Hg⁰ being converted to other forms.^{11,12} The study by Hall et al.¹³ showed that Hg⁰ reacts with Cl₂, HCl, NO₂, and O₂ but not with NH₃, N₂O, SO₂, and H₂S, which means that Hg⁰ could be oxidized by a number of different routes in a real combustion facility.

3.3. Interactions between Mercury and Fly Ash. Much work has shown that vapor-phase emissions of mercury from coal combustion vary considerably over the range 3–70 $\mu\text{g N}^{-1} \text{m}^{-3}$.¹⁴ Some of this variation is accounted for by different coal mercury levels, but the vapor-phase concentration does not always correspond to the Hg content of the coal being burnt, indicating a degree of retention in the dust. Ash plays a role in both the adsorption of mercury and the oxidation of elemental mercury in flue gas. It is this interaction of fly ash particles with mercury vapor that contributes to the final partitioning of mercury. Therefore, it is important to understand the nature of the interaction between fly ash particles and mercury.

It is generally associated with the size differences of the fly ash and/or the surface chemistry of the finer fly ash being enriched in trace metals or another condensed or adsorbed compounds from the flue gas during the combustion of the coal. The mercury concentration of fly ashes with different particle sizes was determined as shown in Figure 6. The scatter in the data suggested that the preferential concentration on a finer fly ash particle has been frequently observed in other trace elements that did not happen. The surface area and pore volumes of fly ash before and after ESPs were also measured by low-temperature nitrogen adsorption using the micrometer analyzer model ASAP 2000 and are given in Table 6. The surface area

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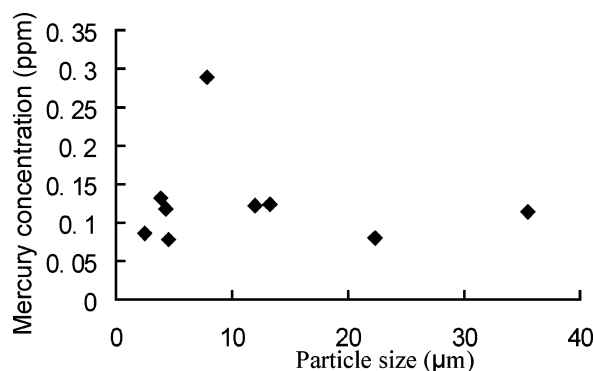


Figure 6. Mercury concentration in fly ashes with a different particle size.

Table 6. BET Result for Fly Ash before and after ESP

sample location	surface area (BET) (m ² /g)	pore volume (cm ³ /g)	average pore diameter (Å)	mercury concentration (μg/g)
before ESP	1.3605	0.004 555	133.9271	0.116
after ESP	1.7707	0.005 277	119.1997	0.086

of the fly ash particle plays an important role in gas–solid reactions. The higher the surface area, the higher the porosity and the higher the accessibility of the fly ash particles to the gaseous reactant. Therefore, on a weight basis, the condensing elements are found in highest concentrations on the smallest particle. If the nature of the capture of mercury on fly ash was explained through a physisorption mechanism, there would be some correlation between the equilibrium capacity of the ash for mercury and surface area. However, the data was opposed to the hypotheses, which suggested that it is not the volatilization of mercury followed by condensation on the total available surface area of fly ashes alone that influences the capture of mercury in fly ash.

The mercury and carbon contents of the dust samples taken at different hoppers of ESPs are shown in Figure 7. It can be seen that surprisingly good correlations of Hg content with loss of ignition (LOI) were observed, which suggested that mercury can be adsorbed by the unburned carbon in the ash and confirm the principle finding of the studies that Hg retention is dependent upon the carbon-in-dust concentration.^{15,16} At a later study, the residual carbon will be separated from fly ash and characterized for surface area, microstructure, and adsorption effect of the different speciation of mercury, etc.

To elucidate the mechanism of mercury and fly ash interaction, Table 7 shows the results of fly ashes vacuumized at 100 °C for 10 h to remove gas in the fly ashes and then absorbed with mercury-free nitrogen gas, after which the fly ashes re-analyzed the mercury concentration. The concentration of

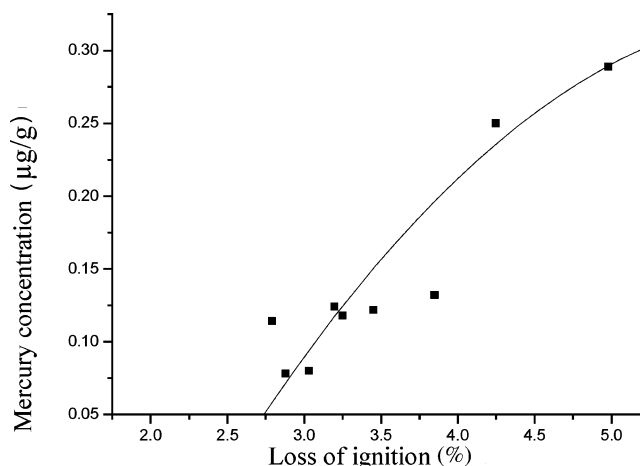


Figure 7. Relationship between mercury retention and carbon-in-dust full scale.

Table 7. Comparison of the Mercury Concentration after Desorption

sample	mercury (μg/g)	after desorption of mercury (μg/g)	desorption (%)
EF-1	0.114	0.102	11
EF-2	0.122	0.079	35.3
EF-3	0.118	0.066	44.1
EF-4	0.132	0.084	36.4
PFA	0.086	0.058	32.6

mercury decreases for all fly ashes after desorption. The percentages of desorption of EF-1, EF-2, EF-3, EF-4, and PFA are 11, 35.3, 44.1, 36.4, 32.6%, respectively. This reversible process indicates that physical adsorption does happen in some sense, which suggests that there may be more than one mechanism by which capture takes place at the postcombustion zone in the case of fly ash, including chemisorption, chemical reaction, and physisorption.

4. Conclusion

To study the behavior of mercury after coal combustion in a power plant, synchronized sampling of pulverized coal, slag, fly ash, and flue gas over a limited period has been conducted. The experimental data indicate that the majority of mercury goes into flue gas and the gaseous mercury concentration in the flue gas after ESP is about 13–21 μg N⁻¹ m⁻³. The mercury concentration in fly ash is independent of the particle size and has a positive correlation with the LOI of fly ash. The absorption mechanism of mercury in fly ash was a combination of chemisorption, chemical reaction, and physisorption.

Acknowledgment. Financial support was sponsored by the National Key Basic Research and Development Program, the Ministry of Science and Technology, China (2006CB200304), and the National Natural Science Foundation of China (NSFC) (90410017 and 50506011).

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