

# Investigation of the Relationship between Particulate-Bound Mercury and Properties of Fly Ash in a Full-Scale 100 MWe Pulverized Coal Combustion Boiler

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The properties of fly ash in coal-fired boilers influence the emission of mercury from power plants into the environment. In this study, seven different bituminous coals were burned in a full-scale 100 MWe pulverized coal combustion boiler and the derived fly ash samples were collected from a mechanical hopper (MH) and an electrostatic precipitator hopper (ESP). The mercury content, specific surface area (SSA), unburned carbon, and elemental composition of the fly ash samples were analyzed to evaluate the correlation between the concentration of particulate-bound mercury and the properties of coal and fly ash. For a given coal, it was found that the mercury content in the fly ash collected from the ESP was greater than in the fly ash samples collected from the MHP. This phenomenon may be due to a lower temperature of flue gas at the ESP (~135 °C) compared to the temperature at the air preheater (~350 °C). Also, a significantly lower SSA observed in MH ash might also contribute to the observation. A comparison of the fly ash samples generated from seven different coals using statistical methods indicates that the mercury adsorbed on ESP fly ashes has a highly positive correlation with the unburned carbon content, manganese content, and SSA of the fly ash. Sulfur content in coal showed a significant negative correlation with the Hg adsorption. Manganese in fly ash is believed to participate in oxidizing volatile elemental mercury (Hg<sup>0</sup>) to ionic mercury (Hg<sup>2+</sup>). The oxidized mercury in flue gas can form a complex with the fly ash and then get removed before the flue gas leaves the stack of the boiler.

## Introduction

Mercury is listed as one of the hazardous air pollutants (HAPs) under Section 112 of the Clean Air Act as amended in 1990. The deposition of mercury from air or surface runoffs is potentially harmful to ecosystems and human health<sup>1–3</sup> because the deposited Hg can be biologically transformed into a highly toxic form (i.e., methylmercury, MeHg). High-dosage exposure from the consumption of MeHg-contaminated fish has been reported to cause fatalities and severe neurological damage.<sup>2,3</sup> Deposition of atmospheric mercury is a growing concern in the United States because mercury has been the chemical contaminant responsible for the number and spatial extent of fish consumption advisories issued.<sup>4</sup>

From 1990 to 1999, anthropogenic mercury emissions have dropped 45% in the United States. However, mercury emission

from coal combustion boilers has been only reduced 6%.<sup>5,6</sup> The coal combustion process remains the largest anthropogenic mercury emission source in the United States.<sup>7</sup> The Clean Air Mercury Rule (CAMR) issued by the U.S. Environmental Protection Agency (EPA) on March 15, 2005 requires the power industry to implement the maximum achievable control technology to reduce mercury emission 20% by 2010 and 50% by 2018.<sup>8</sup>

The chemical species of gaseous mercury in combustion flue gases is an important factor influencing the control of mercury emissions from coal combustion. Elemental mercury is volatile and insoluble in water, which makes it difficult to be removed from flue gas. Oxidized mercury, on the other hand, is water-soluble and easy to associate with particulate matter. It can be absorbed onto fly ash and removed by particulate emission control devices, such as electrostatic precipitators (ESPs), mechanic mechanical hoppers (MHPs), and fabric filters (FFs).

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(1) U.S. Department of Energy, Energy Information Administration. *U.S. Coal Reserves: 1997 Update*. DOE/EIA-0529 (97). Office of Coal, Nuclear, Electric, and Alternate Fuels, Office of Integrated Analysis and Forecasting: Washington, D.C., February 1999.

(2) National Research Council. *Toxicological Effects of Methylmercury*. Committee on the Toxicological Effects of Methylmercury Board on Environmental Studies and Toxicology, Commission on Life Sciences. National Academy Press: Washington, D.C., 2000.

(3) Mishima, A. *Bitter Sea: The Human Cost of Minamata Disease*; Kosei Publishing Co.: Tokyo, Japan, 1992.

(4) U.S. EPA. *Mercury Research Multi-Year Plan*; U.S. Environmental Protection Agency: Washington, D.C., 2003.

(5) Miller, L. Air Toxics and Monitoring Branch, U.S. EPA, Region 4. *Clean Air Mercury Rule*; U.S. Environmental Protection Agency: Washington, D.C., 2005.

(6) U.S. EPA. *Database of Information Collected in the Electric Utility Steam Generating Unit Mercury Emissions Information Collection Effort*. OMB Control No. 2060-0396; Office of Air Quality Planning and Standards: Research Triangle Park, NC, April 2001.

(7) U.S. EPA. *Mercury Study Report to Congress*, Vol. I: Excessive Summary; EPA-452/R-97-003; Office of Air Quality Planning and Standards and Office of Research and Development; U.S. Environmental Protection Agency: Washington, D.C., 1997.

(8) U.S. EPA. *Mercury Regulatory Impact Analysis of the Final Clean Air Mercury Rule*; U.S. Environmental Protection Agency: Washington, D.C., 2003.

Averages of 36 and 90% of mercury removal efficiency have been reported as removable by ESP and FF, respectively.<sup>9</sup>

The adsorption of Hg on fly ash is highly variable depending upon the coal type, boiler configuration, mercury speciation in flue gas, fly ash characteristics, and operational conditions of the air pollution control devices.<sup>10</sup> These variables may affect the catalytic effect of fly ash on the oxidation process of elemental Hg in flue gas and consequently may vary the adsorption of Hg onto fly ash. Many bench- or pilot-scale studies have therefore been carried out to elucidate the effect of flue gas composition and the physical and chemical characteristics of fly ash on the capture of Hg by fly ash.

In the case of flue gas composition, halogens and hydrogen halides (e.g., Cl<sub>2</sub> and HCl) have been observed to effectively promote the oxidation of elemental Hg in numerous laboratory studies. The oxidation process of elemental Hg in flue gas can consequently increase the chance for fly ash particles to capture oxidized Hg. Norton et al.<sup>11</sup> found that, with a simulated flue gas stream containing 50 ppm of HCl, over 25% of the elemental Hg can be oxidized in the presence of NO<sub>2</sub>. Lee et al.<sup>12</sup> observed that 100% of the elemental Hg was oxidized to HgCl<sub>2</sub> in less than 2 s at 40 °C and in the presence of 50 ppm of Cl<sub>2</sub>. They also found that the oxidation of Hg<sup>0</sup> in the presence of HCl was slow at low to moderate temperatures (25–350 °C).<sup>12,13</sup> Contrary to the potential promotion effect of HCl, the presence of nitrogen monoxide (NO),<sup>11</sup> sulfur dioxide (SO<sub>2</sub>),<sup>14,15</sup> and moisture (H<sub>2</sub>O)<sup>14</sup> in flue gas appears to inhibit the oxidation of Hg<sup>0</sup> over model or real fly ashes.

In addition to the composition of flue gas, the correlation between the chemical and mineral compositions of fly ash and mercury adsorption has also been studied. Lee and colleagues<sup>13,12</sup> observed that cupric and iron oxides were the two components that exhibited significant catalytic activity in the oxidation of Hg<sup>0</sup> in a study using model fly ashes composed of mixtures of Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, CuO, and CaO. Similar results were also observed by Dunham et al.,<sup>16</sup> who investigated the adsorption of elemental Hg and HgCl<sub>2</sub> on 16 different fly ash samples in a bench-scale reactor using a simulated flue gas. They concluded that the oxidation of elemental Hg increased with an increasing amount of magnetite in the ash. Besides the catalytic effect induced by the mineral/elemental composition of fly ash, Thorwarth et al.<sup>17</sup> suggested that high contents of CaO and MgO in fly ash can increase the adsorption of Hg on fly ash.

However, Norton et al.<sup>18</sup> suggested that the chemical and mineralogical differences between fly ashes may not play a significant role upon reacting with Hg<sup>0</sup>. They proposed the difference in reactivity could be largely due to the surface area of fly ash samples tested in their study. A similar conclusion was also drawn by Dunham et al.,<sup>16</sup> who observed that the adsorption of Hg on fly ash has a good correlation with the surface area. However, the correlation between Hg adsorption and loss on ignition (LOI) was not as strong in their study, which is different from what was observed by other researchers. Hassett and Eylands,<sup>19</sup> for example, found a direct correlation between carbon content and mercury partition among individual ash samples. They also suggested that the adsorption of Hg on the inorganic fraction of fly ash is extremely low compared to carbon present in the ash.

Despite many factors controlling the capture of Hg by fly ash, the relative importance is still not clear. The ash samples used in the above studies were generated from different operational conditions. These conditions might have played important roles in contributing to the reactivity of the ashes, and thus, affecting the capture of Hg by fly ash. In addition, the current investigations are limited to bench- or pilot-scale field testing. The time and temperature involved for the transformation of mercury in a full-scale boiler are not always completely simulated in bench- or pilot-scale combustion systems.

In this study, the correlation between fly ash properties and the fraction of particulate-bound mercury was studied by a full-scale, commercially operated coal combustion boiler with six different bituminous coals. The chemical compositions and properties of the ash samples were analyzed, and a statistical model was built to predict the correlations based on the regression of the analytical results.

## Experimental Section

This study was conducted in a full-scale 100 MWe pulverized coal-firing facility, which has a front wall-fired, low NO<sub>x</sub> burner. A cold-side electrostatic precipitator (ESP) is used as a particulate-control device. No sulfur dioxide emission control unit is available in the testing power plant.

**Coal and Fly Ash.** Seven bituminous coals tested in this study were obtained from different sources with various mercury, chlorine, and sulfur contents. Fly ash samples were collected from two discharge locations, i.e., mechanical hoppers after the air preheater and hoppers associated with the ESP.

**Analytical Methods.** The mercury contents in the coal and fly ash samples were analyzed using a LECO AMA-254 mercury analyzer (LECO Instruments, Ltd., MI). Approximately 0.2–1 g of coal and ash sample was used for analysis. The mercury content was measured by a standard atomic adsorption spectrometer after the sample was directly combusted in an oxygen-rich environment.

The unburned carbon content in fly ash was analyzed using a LECO CHN2000 analyzer (LECO Instruments, Ltd., MI) as per American Society for Testing and Materials (ASTM) D5373.<sup>20</sup> An autoloader was used to handle the sample throughput after weighing. Before starting the LOI analysis, the instrument was calibrated with blanks and National Institute of Standards and Technology (NIST)

(9) Yudovich, Ya. E.; Ketris, M. P. *Int. J. Coal Geol.* **2005**, *62*, 135–165.

(10) Senior, C. L. *Energy Fuels* **2005**, *19*, 859–863.

(11) Norton, G. A.; Yang, H.; Brown, R. C.; Laudal, D. L.; Dunham, G. E.; Erjavec, J. *Fuel* **2002**, *82*, 170–176.

(12) Lee, C. W.; Kilgroe, J. D.; Ghorishi, S. B. Mercury control research: Effects of fly ash and flue gas parameters on mercury speciation. 6th Annual Waste-to-Energy Conference, Proceedings of a Specialty Conference, Miami Beach, FL, May 11–13, 1998; pp 221–238.

(13) Ghorishi, S. B.; Lee, C. W.; Kilgroe, J. D. Mercury speciation in combustion systems: Studies with simulated flue gases and model fly ashes. Presented at the 92nd Annual Meeting of Air and Waste Management Association, St. Louis, MO, June 20–24, 1999.

(14) Lee, C. W.; Srivastava, R. K.; Kilgroe, J. D.; Ghorishi, S. B. Effects of iron content in coal combustion fly ashes on speciation of mercury. Proceedings of the Air and Waste Management Association's 94th Annual Conference and Exhibition, Orlando, FL, June 24–28, 2001; pp 1374–1388.

(15) Serre, S. D.; Silcox, G. D. *Ind. Eng. Chem. Res.* **2000**, *39*, 1723–1730.

(16) Dunham, G. E.; DeWall, R. A.; Senior, C. L. *Fuel Process. Technol.* **2003**, *82*, 197–213.

(17) Thorwarth, H.; Stack-Lara, V.; Unterberger, S.; Scheffknecht, G. The influence of fly ash constituents on mercury speciation. Proceedings of Air Quality V, Washington, D.C., September 19–21, 2005.

(18) Norton, G. A.; Yang, H.; Brown, R. C.; Laudal, D. L.; Dunham, G. E.; Erjavec, J.; Okoh, J. M. Role of fly ash on mercury chemistry in simulated flue gas streams. Proceedings of the Air and Waste Management Association's 94th Annual Conference and Exhibition, Orlando, FL, June 24–28, 2001; pp 1389–1407.

(19) Hassett, D.; Eylands, K. E. *Fuel* **1999**, *78*, 243–248.

(20) American Society for Testing and Materials. ASTM Designation: D 5373-02, Standard Test Methods for Instrumental Determination of Carbon, Hydrogen, and Nitrogen in Laboratory Samples of Coal and Coke; ASTM: West Conshohocken, PA, 2002.

**Table 1. Mercury Concentration in Coal and Fly Ash Samples**

sample	Hg in coal (mg/g)	Hg in MH <sup>a</sup> ash		Hg in ESP <sup>b</sup> ash	
		concentration (mg/g)	Hg <sub>MH ash</sub> /Hg <sub>coal</sub> <sup>c</sup>	concentration (mg/g)	Hg <sub>ESP ash</sub> /Hg <sub>coal</sub> <sup>c</sup>
coal #1	0.12	0.09	0.75	0.41	3.42
coal #2	0.10	0.06	0.60	0.30	3.00
coal #3	0.11	0.11	1.00	0.59	5.36
coal #4	0.13	0.23	1.77	1.11	8.54
coal #5	0.06	0.12	2.00	0.99	16.5
coal #6	0.12	0.11	0.92	0.67	5.58
coal #7	0.24	0.09	0.38	0.30	1.25

<sup>a</sup> MH ash = ash collected from the mechanical hopper. <sup>b</sup> ESP ash = ash collected from the ESP hopper. <sup>c</sup> Calculated by dividing Hg in MH ash or Hg in ESP ash by Hg in coal.

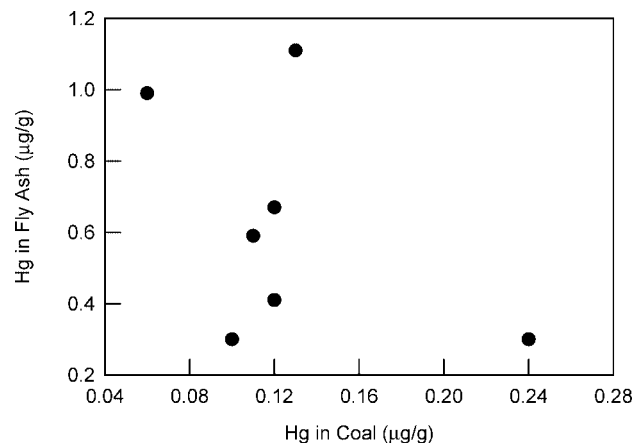
standard reference material, 1633b. Each sample was measured in duplicate, and the mean value was reported.

A LECO AC350 (LECO Instruments, Ltd., MI) was used for measuring the calorific value of coal samples and preparing the samples for chlorine analysis. Benzoic acid pellets were used to calibrate the AC350 instrument before analysis. The procedure was repeated every 10 samples to assure the calibration validation. Each sample was measured in duplicate. For Cl analysis, 1  $\mu$ L of the solution prepared by the AC350 instrument was injected into a Dionex DX 120 ion chromatograph (Dionex Co., CA).

The sulfur content in coal and fly ash was measured using a LECO SC432 (LECO Instruments, Ltd., MI) according to ASTM D4239.<sup>21</sup> The analysis was carried out at 1350 °C under an oxygen atmosphere. The instrument was calibrated using standard samples before the each test. Approximately 200 mg of coal or ash samples were weighed, put into the ceramic boat, and then loaded into the instrument. Each sample was measured twice to ensure reproducibility.

A TGA-601 instrument (LECO Instruments, Ltd., MI) was used to measure the LOI values for the ash samples collected from the mechanical hopper and ESP hopper as per standard method ASTM D5142.<sup>22</sup> The moisture content was also determined during the LOI analysis. An X-ray fluorescence (XRF) instrument (Rigaku RIX 3001, Rigaku America, TX) was used to analyze the trace elements in coal and fly ash samples. Before the XRF analysis, the samples were preheated to oxidize all carbonaceous material and decompose minerals containing carbonates, sulfides, and hydroxides in the atmosphere. After the pretreatment, the glass pellets used for XRF analysis were prepared following ASTM methods D-3682<sup>23</sup> and D-4326.<sup>24</sup> The XRF instrument was calibrated with the standard baseline built in the method. The concentrations of Al<sub>2</sub>O<sub>3</sub>, MnO<sub>2</sub>, SrO, Na<sub>2</sub>O, MgO, SiO<sub>2</sub>, CaO, K<sub>2</sub>O, SO<sub>3</sub>, P<sub>2</sub>O<sub>5</sub>, BaO, Fe<sub>2</sub>O<sub>3</sub>, and TiO<sub>2</sub> were measured.

The specific surface area (SSA) of fly ash samples was analyzed using the ethylene glycol monoethyl ether (EGME) method first developed by Eltantawy and Arnold.<sup>25</sup> In summary, a CaCl<sub>2</sub>-EGME solvate was made by mixing 20 g of EGME in a 100 g of hot calcium chloride solution. The mixture was then dried at 210 °C for 1 h. After the solvate had cooled, it was transferred to a culture chamber and spread uniformly over the bottom. To measure the surface area, each ash sample was first saturated with calcium ions by leaching with an excess of 1.0 M CaCl<sub>2</sub>. The treated fly ash sample was then air-dried after the excess CaCl<sub>2</sub> was removed by



**Figure 1.** Comparison of the mercury concentration in fly ash with the mercury concentration in coal.

rinsing with deionized water and then passed through a 60-mesh sieve. Approximately 1.1 mg of pretreated ash sample was weighed and placed into an aluminum can with a lid. The sample was then dried in an oven at 110 °C for 24 h. The oven-dried samples were wetted with 3 mL of EGME after weighing. The cans were placed in the culture chamber with CaCl<sub>2</sub>-EGME, and the entire culture chamber was placed in a vacuum desiccator containing CaCl<sub>2</sub>. The desiccators were evacuated by applying a vacuum pump for about 45 min. After the sample stayed in the desiccators for 4–6 h, the sample was weighed again. The procedure of evacuating–standing–weighing was repeated several times until the weight change was less than 0.1 mg between successive weighing. The SSA was calculated using the following equation:

$$A = \frac{W_a}{(W_s \times 0.000286)} \quad (1)$$

where  $A$  is the SSA in m<sup>2</sup>/g,  $W_a$  is the weight of EGME retained in the sample in grams,  $W_s$  is the weight of the oven-dried sample in grams, and 0.000286 is the weight of EGME required to form a monomolecular layer on a square meter of surface.

## Results and Discussions

**Particulate-Bound Mercury.** The mean values of the Hg contents in the coal tested in this study and in the fly ash samples collected from the mechanical hopper (MH) and ESP hopper for each tested coal are shown in Table 1. As can be seen, the mercury concentrations in the coals were in a range of 0.06–0.24 ppm. For ash samples collected from ESP and mechanical hoppers, the mercury concentrations were found to be in a range from 0.30 to 1.10 ppm and from 0.06 to 0.23 ppm, respectively.

First, the correlation between Hg in ash and Hg in coal was examined, and the results are shown in Figure 1. As can be seen, the Hg concentration in ESP ash or MH ash does not correspond to the mercury content in the coal. When the Hg content in coal was regressed against the Hg content in the two

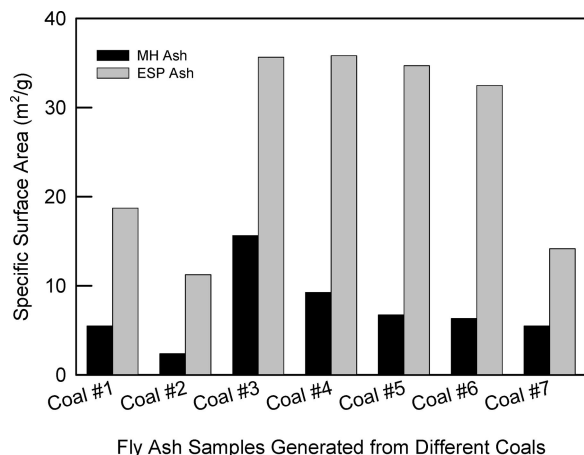
(21) American Society for Testing and Materials. ASTM Designation: D 4239-04, Standard Test Methods for Sulfur in the Analysis Sample of Coal and Coke Using High-Temperature Tube Furnace Combustion Methods; ASTM: West Conshohocken, PA, 2004.

(22) American Society for Testing and Materials. ASTM Designation: D 5142-04, Standard Test Methods for Proximate Analysis of the Analysis Sample of Coal and Coke by Instrumental Procedures; ASTM: West Conshohocken, PA, 2004.

(23) American Society for Testing and Materials. AASTM Designation: D 3682-01, Standard Test Method for Major and Minor Elements in Combustion Residues from Coal Utilization Processes; ASTM: West Conshohocken, PA, 2001.

(24) American Society for Testing and Materials. ASTM Designation: D 4326-04, Standard Test Method for Major and Minor Elements in Coal and Coke Ash by X-ray Fluorescence; ASTM: West Conshohocken, PA, 2004.

(25) Eltantawy, I. M.; Arnold, P. W. *J. Soil Sci.* **1973**, *24*, 232–238.



**Figure 2.** Comparison of the SSA of fly ash samples collected from the mechanical hopper and ESP hopper.

types of ashes, it was found that the  $p$  values for MH ash and ESP ash were 0.903 and 0.302. The results indicated that there are 90.3 and 30.2% chances that there is no correlation between the Hg in coal and Hg in ash. The observation confirms that other chemical properties of coal and/or fly ash may play a more important role in controlling the adsorption of Hg on both types of fly ashes.

To compare the effects of the coal and ash properties on the adsorption of Hg on fly ash, a Hg concentration factor (i.e., Hg CF) was used, which was calculated by dividing the concentrations of Hg in the ash samples collected from both the ESP and mechanical hoppers by the concentration of Hg in the respective coal. The results are summarized in Table 1. As can be seen in the table, the Hg CF values range from 0.375 to 2.0 for the MH ash and it increase to  $\sim 1.25$ – $16.5$  in the case of the ESP ash. The higher Hg CF values observed in the ESP fly ash might be due to a lower temperature of flue gas at the ESP ( $\sim 135$  °C) compared to the temperature at the air preheater ( $\sim 350$  °C). In addition to the temperature, the significant difference found in the SSA of the two types of ashes (Figure 2) might also contribute to the observation. As can be seen in Figure 2, the SSA of MH fly ash was found to be much less than the SSA of ESP fly ash. It was found that SSA of ESP fly ash plays a significant role in the adsorption of Hg. A detailed discussion can be seen in the SSA session.

The unburned carbon or LOI of the MH ash was very close or even higher than what was found in the ESP ash; therefore, unburned carbon content or LOI is unlikely to be responsible for the observed Hg concentration difference on ESP and MH ashes. Detailed physical and chemical properties of MH ash and ESP ash can be seen in Table 2.

**Effect of Coal Properties.** The correlation between the properties of coal and Hg concentrations in ashes was first examined. The chemical characteristics of the coals tested in this study are summarized in Table 3. Figure 3 plots the concentrations of F, Cl, S, and moisture in the tested coals as a function of the Hg CF values for the two types of ashes. The regression results obtained from the statistics software SPSS 13.0 are shown in Tables 4 and 5 for MH and ESP ashes, respectively. The regression was done twice by including and excluding coal sample #5. It was found that the ESP fly ash sample obtained from coal #5 has a much higher Hg CF value (16.5) than other ash samples (ranging from 1.25 to 8.58). Considering that regression results can be significantly affected by the data that is far away from the others and lead to misinterpreting the correlation, the regression was performed twice to evaluate the effect of coal #5 on the regression results.

As can be seen in Tables 4 and 5, for both types of fly ashes (i.e., MH and ESP ash), all selected statistic parameters show no strong correlation between the halogen contents in coal and the concentration of Hg in ash. It is true for both regression cases, in which coal sample #5 was included (the “all” column in the tables) and excluded (the “excluded” column in the tables). The reaction of  $\text{Hg}^0$  with halogen, Cl in particular (either in its halogen, hydrogen halide, or atom forms), to form  $\text{HgCl}_{2(g)}$  is generally considered to be the major mercury transformation mechanism in coal combustion flue gas. The reason that no significant correlation between the halogen contents and the Hg adsorption observed in this study is likely due to the high Cl contents in the coals tested in this study. Results from a previous study,<sup>26</sup> in which the correlation between Hg species in flue gas and Cl contents in the coals was investigated, suggested that the oxidation of elemental Hg may have reached a maximum when chlorine content in the coal is higher than 1000 ppm. Therefore, the adsorption of resulting oxidized Hg on fly ash was controlled by other coal and/or fly ash properties in this study.

The conclusion obtained from a previous study<sup>27</sup> stating that chlorine promotes the chemisorption of mercury onto fly ash is not found in this study. It is due to the variables selected by the two studies. In the previous study, the conclusion was drawn because the chlorine concentration in the coal was found to have a negative correlation with the Hg concentration in flue gas. However, when the Hg concentrations in both fly ash and coal were further studied in this paper, it was found that the effect of chlorine on the adsorption of Hg on fly ash is not significant.

In the case of sulfur, no correlation was observed between the S content and Hg concentration in MH ash in both regression cases. The same observation was found for the ESP ash when including all of the 7 coal samples in the regression. However, a negative correlation was observed when sample #5 was excluded from the regression. The  $F$ -statistic values significantly increased from 1.186 to 7.568 along with the decrease of the  $p$  value from 0.326 to 0.051 as sample #5 was excluded. The  $F$  statistic, also known as the  $F$  ratio, is a measure for the strength of the regression. When the  $F$ -statistic value is larger and the  $p$  value is lower, a stronger correlation between the two variables is indicated. It was also found that the Pearson correlation coefficient was changed from  $-0.438$  to  $-0.803$ . A negative Pearson correlation coefficient indicates reverse correlation between the two variables.

The effect of S in coal on the adsorption of Hg in fly ash has been suggested by other researchers.<sup>15,28</sup> In a bench-scale study conducted by Serre and Silcox,<sup>15</sup> the presence of sulfur dioxide was found to reduce 40% of the amount of  $\text{Hg}^0$  adsorbed on fly ash. They suggested that the observed inhibition effect of  $\text{SO}_2$  on the adsorption of Hg by fly ash was due to adsorption site competition.<sup>15</sup> Galbreath and Zygarlicke,<sup>28</sup> however, suggested that a high sulfur/chlorine ratio of coal can inhibit the formation of  $\text{Cl}_2$  and subsequently that of  $\text{HgCl}_2$ , which results in low Hg adsorption on fly ash. The  $\text{Cl}_2$ -scavenging mechanism was found to be insignificant in this study. The Pearson correlation coefficient between the Hg CF value of the ESP fly ash and the ratio of S/Cl in coal was found to be 0.15.

As shown in Table 5, the “all” columns revealed that the moisture content has a strong correlation with the Hg concentra-

(26) Cao, Y.; Duan, Y.; Kellie, S.; Li, L.; Xu, W.; Riley, J. T.; Pan, W.-P.; Chu, P.; Mehta, A. K.; Carty, R. *Energy Fuels* **2005**, *19*, 842–854.

(27) Kellie, S.; Cao, Y.; Duan, Y.; Li, L.; Chu, P.; Mehta, A.; Carty, R.; Riley, J.; Pan, W.-P. *Energy Fuels* **2005**, *19*, 800–806.

(28) Galbreath, K. C.; Zygarlicke, C. J. *Fuel Process. Technol.* **2000**, *65–66*, 289–310.

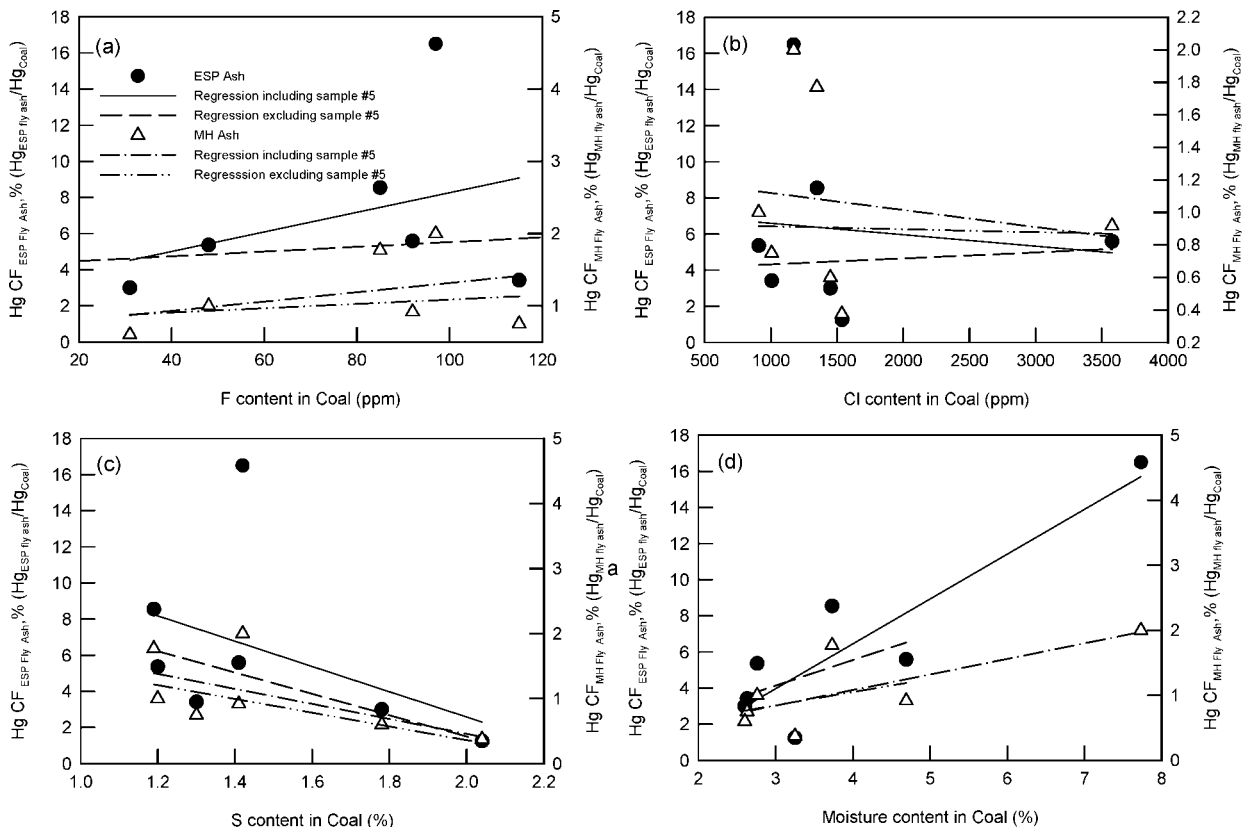


Figure 3. Correlation between the Hg CF ( $Hg_{fly\ ash}/Hg_{coal}$ ) values to (a) fluorine, (b) chlorine, (c) sulfur, and (d) moisture content in coal.

Table 2. Surface Area and Chemical Properties of Fly Ash Samples Prepared from Coals Used in This Study

	unit	coal #1		coal #2		coal #3		coal #4		coal #5		coal #6		coal #7	
		MH	ESP	MH	ESP	MH	ESP	MH	ESP	MH	ESP	MH	ESP	MH	ESP
surface area	m <sup>2</sup> /g	5.48	18.7	2.36	11.23	15.63	35.64	9.25	35.82	6.72	34.69	6.31	32.46	5.48	14.16
unburned carbon	%	5.21	4.91	4.07	3.9	7.80	5.3	9.52	6.57	6.79	6.89	5.60	3.9	2.06	2.41
LOI	%	5.50	5.84	4.08	5.17	8.40	6.51	11.69	7.56	6.84	7.72	6.76	5.12	3.07	3.44
S	%	0.11	0.62	0.11	0.63	0.25	0.47	0.20	0.57	0.11	0.41	0.18	0.67	0.10	0.59
Cl	%	130	107	100	127	79	132	141	222	169	221	510	530	189	200
F	%	50	195	36	610	57	149	262	303	28	107	83	181		

Table 3. Characteristics of Coals

	unit	coal #1	coal #2	coal #3	coal #4	coal #5	coal #6	coal #7
Btu	Btu/lb	13 309	13 257	13 196	13 544	13 783	13 530	12 459
moisture	%	2.63	2.60	2.76	3.73	7.73	4.69	3.25
ash content	%	9.60	9.89	9.63	8.61	10.93	8.37	16.20
volatile material	%	32.89	32.86	35.89	36.39	38.57	37.81	36.12
sulfur	%	1.30	1.78	1.20	1.19	1.42	1.66	1.58
carbon	%	75.79	75.84	74.81	75.18	75.18	76.58	68.89
hydrogen	%	5.00	5.04	4.83	4.88	4.47	5.64	4.81
nitrogen	%	1.77	1.66	1.58	1.67	1.42	1.66	1.58
oxygen	%	6.54	5.78	7.95	8.03	6.58	6.34	6.48
chloride	ppm	1006	1449	908	1348	1171	3577	1536
fluoride	ppm	115	31	48	85	97	92	

tion in the ESP ash; however, this correlation was not observed if sample #5 was excluded from the regression. The effect of moisture in coal on the adsorption of fly ash is not clear and has rarely been discussed. Yudovich and Ketris<sup>9</sup> suggested that the feed coal moisture might have an adverse effect on the formation of Cl<sup>-</sup>, which implies an inhibition effect on the formation of HgCl<sub>2</sub>. On the other hand, the coal moisture can help create active surface functional groups on the fly ash particles, which can promote Hg adsorption. Higgins et al.<sup>29</sup>

reviewed the studies that had used X-ray near-edge structure (XANES) spectroscopy to study the speciation of Hg on fly ash. They concluded that mercury can be captured by bonding to I, Cl, S, or O anionic species on the surfaces of the carbonaceous fraction of fly ash.<sup>29</sup> The increase of the moisture content in flue gas might increase the number of surface active sites (e.g., -OH) available for mercury adsorption. A further investigation is needed to elucidate the effect of feed coal moisture on the transformation of Hg in flue gas.

**Fly Ash Properties. Carbon Content.** The correlation of the mercury concentration and unburned carbon in both MHP and ESP

(29) Huggins, F. E.; Yap, N.; Huffman, G. P.; Senior, C. L. *Fuel Process. Technol.* **2003**, *82*, 167–196.

**Table 4. Regression Analysis Results (Mechanical Hopper Ash)**

variables	Pearson correlations		R <sup>2</sup>		F statistic		p value	
	all	excluded	all	excluded	all	excluded	all	excluded
coal properties								
Cl	0.159	-0.037	0.025	0.001	0.130	0.005	0.734	0.945
F	0.359	0.225	0.129	0.051	0.591	0.160	0.485	0.716
moisture	0.730	0.346	0.553	0.120	5.716	0.545	0.062	0.501
S	-0.608	-0.765	0.370	0.586	2.938	5.651	0.147	0.760
ash properties								
C	0.789	0.942	0.623	0.888	8.253	31.718	0.035	0.005
LOI	0.734	0.980	0.539	0.960	5.853	95.668	0.06	0.001
SSA	0.300	0.474	0.090	0.225	0.496	1.159	0.513	0.342
S	0.247	0.668	0.061	0.447	0.326	3.229	0.59	0.147
Cl	0.062	-0.030	0.004	0.001	0.019	0.004	0.90	0.954
F	-0.525	-0.969	0.376	0.940	1.925	62.141	0.23	0.001
Na <sub>2</sub> O	0.093	0.048	0.009	0.002	0.044	0.009	0.84	0.928
MgO	0.332	0.590	0.110	0.348	0.617	2.139	0.47	0.217
Al <sub>2</sub> O <sub>3</sub>	0.399	0.503	0.159	0.253	0.947	1.355	0.38	0.309
SiO <sub>2</sub>	0.145	0.505	0.021	0.003	0.107	0.010	0.76	0.925
CaO	0.138	0.163	0.019	0.027	0.097	0.110	0.77	0.757
K <sub>2</sub> O	0.605	0.582	0.366	0.339	2.880	2.050	0.15	0.225
SO <sub>3</sub>	0.146	0.001	0.021	0.000	0.109	0.000	0.75	0.999
P <sub>2</sub> O <sub>5</sub>	0.605	0.756	0.366	0.571	2.891	5.331	0.15	0.082
BaO	0.228	0.108	0.052	0.012	0.273	0.048	0.62	0.838
SrO	0.558	0.743	0.311	0.553	2.256	4.939	0.19	0.090
Fe <sub>2</sub> O <sub>3</sub>	0.277	0.223	0.077	0.050	0.416	0.210	0.55	0.671
MnO <sub>2</sub>	0.701	0.883	0.492	0.780	4.842	14.168	0.08	0.020
TiO <sub>2</sub>	0.688	0.382	0.474	0.146	4.499	0.683	0.09	0.455

**Table 5. Regression Analysis Results (ESP Ash)**

variables	Pearson correlations		R <sup>2</sup>		F statistic		p value	
	all	excluded	all	excluded	all	excluded	all	excluded
coal properties								
Cl	0.114	0.128	0.013	0.016	0.066	0.067	0.807	0.809
F	0.345	0.203	0.119	0.041	0.539		0.504	
S	-0.438	-0.809	0.192	0.654	1.186	7.568	0.326	0.051
moisture	0.898	0.454	0.806	0.206	20.734	1.040	0.006	0.365
ash properties								
C	0.831	0.864	0.691	0.747	11.159	11.800	0.021	0.026
LOI	0.811	0.877	0.657	0.769	9.57	13.311	0.027	0.022
SSA	0.679	0.867	0.461	0.752	4.274	12.124	0.094	0.025
S	-0.723	0.218	0.524	0.048	5.50	0.200	0.066	0.678
Cl	0.138	0.296	0.019	0.087	0.10	0.383	0.768	0.569
F	0.164	0.148	0.027	0.022	0.14	0.089	0.725	0.780
Na <sub>2</sub> O	0.001	0.312	0.000	0.098	0.000	0.432	0.998	0.547
MgO	-0.273	0.044	0.074	0.002	0.401	0.008	0.554	0.934
Al <sub>2</sub> O <sub>3</sub>	0.059	0.216	0.003	0.047	0.017	0.198	0.900	0.681
SiO <sub>2</sub>	0.291	0.047	0.085	0.002	0.462	0.009	0.527	0.929
CaO	-0.052	0.168	0.003	0.029	0.013	0.118	0.912	0.749
K <sub>2</sub> O	0.213	0.029	0.045	0.001	0.238	0.003	0.646	0.957
SO <sub>3</sub>	-0.145	0.146	0.021	0.021	0.108	0.087	0.756	0.782
P <sub>2</sub> O <sub>5</sub>	-0.710	0.410	0.504	0.168	5.071	0.807	0.074	0.420
BaO	-0.262	0.074	0.069	0.005	0.369	0.022	0.570	0.889
SrO	-0.554	0.463	0.307	0.214	2.217	1.091	0.197	0.365
Fe <sub>2</sub> O <sub>3</sub>	0.239	0.136	0.057	0.019	0.303	0.760	0.606	0.797
MnO <sub>2</sub>	0.769	0.950	0.592	0.903	7.255	37.430	0.043	0.004
TiO <sub>2</sub>	0.111	0.146	0.012	0.021	0.063	0.088	0.812	0.782

ash are shown in Figure 4. According to the regression results summarized in Tables 4 (MH ash) and 5 (ESP ash), it was observed that the carbon content has a strong positive correlation to the Hg concentration for both types of ash. When including coal sample #5 in the regression, the Pearson correlation coefficient was found to be 0.789 and 0.831 for MH and ESP ashes, respectively. High *F*-statistic values (8.253 for MH ash and 11.159 for ESP ash) and lower than 0.05 for the *p* values (0.035 and 0.021 for MH and ESP ashes, respectively) indicate the significance of the correlations. This linear correlation is more significant as coal sample #5 is excluded (Figure 4a).

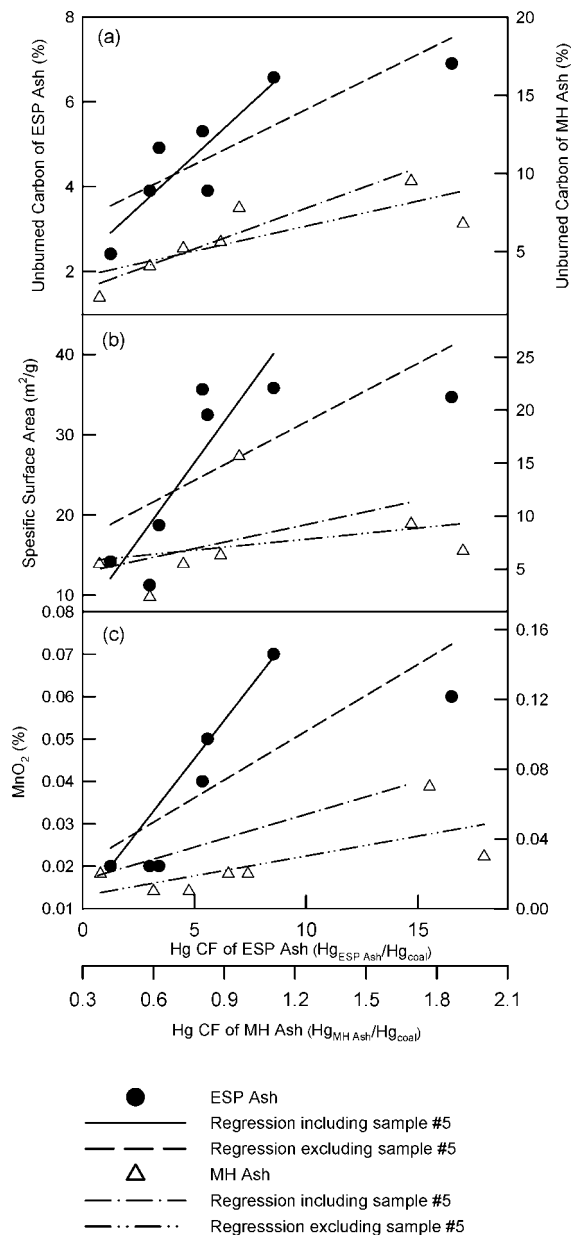
The relationship between the unburned carbon in fly ash and Hg adsorption has been observed by many researchers. In

general, a positive correlation was found.<sup>9,30,31</sup> However, a first-order linear relationship between the adsorption of Hg and the LOI or unburned carbon is not always observed.<sup>10,32</sup> Senior<sup>10</sup> reviewed mercury removal data collected from five full-scale cold-side ESPs and applied a second-order polynomial fit for those data. A yield of *R*<sup>2</sup> of 0.56 was obtained. A nonlinear correlation between the unburned carbon content and the Hg concentration in fly ash observed from data collected from full-

(30) Sakulpitakphon, T.; Hower, J. C.; Trimble, A. S.; Schram, W. H.; Thomas, G. *Energy Fuels* **2000**, *14*, 727-733.

(31) Bartonova, L.; Klika, Z.; Spears, D. A. *Fuel* **2007**, *86*, 455-463.

(32) Gibb, W. H.; Clarke, F.; Mehta, A. K. *Fuel Process. Technol.* **2000**, *60-65*, 365-377.



**Figure 4.** Regression plot of Hg CF values ( $Hg_{fly\ ash}/Hg_{coal}$ ) and (a) unburned carbon/LOI, (b) SSA, and (c)  $MnO_2$  content.

scale facilities is likely due to the complexity of the adsorption of Hg by the fly ash, such as the variation of operating conditions among facilities as well as the analytical methods applied.

**Surface Area.** The correlation between the SSA and Hg CF in fly ash is shown in Figure 4b for ESP and MH ashes, respectively. The regression results can be seen in Tables 4 and 5. The results demonstrate that the adsorption of the Hg concentration on these two types of fly ash have a different correlation with the SSA. In the case of ESP ash, it was found that the Hg concentration in fly ash seemed to be higher as the SSA of the ash increased. This correlation was more significant when coal sample #5 was not included in the regression, in which the Pearson coefficients increased from 0.679 to 0.867 and the  $p$  values decreased from 0.094 to 0.025. Different from the ESP ash, the regression parameters shown in Table 4 suggest that the Hg concentration in MH ash was not related to the SSA of the ash.

Although, for the ESP ash, the adsorption of Hg on fly ash is strongly related to both unburned carbon and the SSA, it was not due to collinearity. The SSA of the ESP ash showed an

insignificant relationship with the unburned carbon content. The Pearson correlation coefficient was found to be 0.683 when sample #5 is excluded from the regression and 0.742 when it is included. The observed noncorrelated relationship of the SSA and unburned carbon observation agrees with what was observed by other researchers. By studying the LOI and SSA of the bituminous ESP ashes collected from nine full-scale facilities, Dunham et al.<sup>16</sup> found that the surface area of the full-scale ash samples did not appear to follow the carbon content.

According to Kūlaots et al.,<sup>33</sup> the large particle size fractions of fly ash derived from bituminous coal are essentially all unburned carbon and small particle-sized fractions are dominated by mineral particles with small portions of unburned carbon particles. The positive correlation of both unburned carbon and the SSA with the adsorption of Hg in fly ash suggested that (1) the adsorption of Hg on the coarser fraction of the fly ash is likely due to unburned carbon, which has more porosity and can scavenge Hg in its volume,<sup>9</sup> through chemisorption and physical interception, and (2) the mineral compositions and unburned carbon in the finer fraction of the fly ash can also capture Hg in flue gas through surface interaction, e.g., adsorption.

When fly ash in flue gas passes through the ESP unit, the small particle ash is much easier to be charged and collected by the ESP plates because of its smaller size and mass. The charged ESP ash may accumulate and aggregate to form a porous ash particle with a high SSA. On the other hand, more active sites for the adsorption of other chemicals in flue gas, such as sulfur, chlorine, and manganese, are available on the larger surface of the charged fly ash. Therefore, a linear regression relationship between SSA and particulate mercury in ESP fly ash is well-observed.

Unlike the ESP fly ash, the adsorption of Hg on the MH ash showed a strong correlation with the unburned carbon but not with the SSA. The relationship between the SSA and MH ash was found to be correlated when sample #5 was not added in the regression. The correlation coefficient is calculated to be 0.979 compared to 0.647 when sample #5 is included. The poor correlation between the Hg content and SSA at MH ash might be a result of too low of a mercury concentration that was captured by the MH ash.

**Elemental Composition.** The significance of the correlation between Hg adsorption and the elemental compositions of ESP fly ash can be seen in Table 4. It was found that only the manganese oxide has a high correlation with the adsorption of mercury of both MH ash and ESP ash. The conclusion is based on the high Pearson correlation coefficient,  $R^2$ , and  $F$ -statistics values, with low  $p$  values. The strong correlation was shown in both regression cases (i.e., including and excluding sample #5) for the ESP ash.

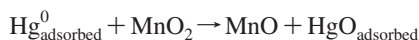
Similar to the correlation observed in this study, Ghorishi et al.<sup>13</sup> found that both  $SiO_2$  and  $Al_2O_3$  were inactive in mercury capture. However, they observed that  $Ca(OH)_2$  effectively captured  $HgCl_2$ .<sup>13</sup> The regression results observed from this study showed that there is no relationship between CaO and the concentration of Hg, which indicates that  $Ca(OH)_2$  is not present as one of the mineral compositions in fly ash.

Recent studies indicate that some manganese compounds have been applied in the development of sorbent techniques.<sup>34</sup> Manganese oxide is believed to be an excellent oxidizing catalyst to oxidize the gaseous elemental mercury into oxidized mercury,

(33) Kūlaots, I.; Hurt, R. H.; Suuberg, E. M. *Fuel* **2004**, *83*, 223–230.

(34) Granite, J. E.; Pennline, W. H.; Hargis, A. R. *Ind. Eng. Chem. Res.* **2000**, *39*, 1020–1029.

and then, the oxidized mercury becomes absorbed into fly ash. Therefore, the strong correlation of manganese oxide and the Hg concentration might be described as an adsorption/oxidation reaction, which can be illustrated by a Mars–Maessen mechanism suggested by Granite et al.<sup>34</sup>



**Sulfur, Chlorine, and Fluorine Contents of Fly Ash.** The correlation between the sulfur, chlorine, and fluorine contents in fly ash and Hg adsorption was also studied. The regression results can be seen in Tables 4 and 5. It was found that the S, Cl, and F contents in fly ash did not show obvious linear correlations with the Hg adsorption. Other characteristics of fly ash have played a more important role in influencing Hg adsorption.

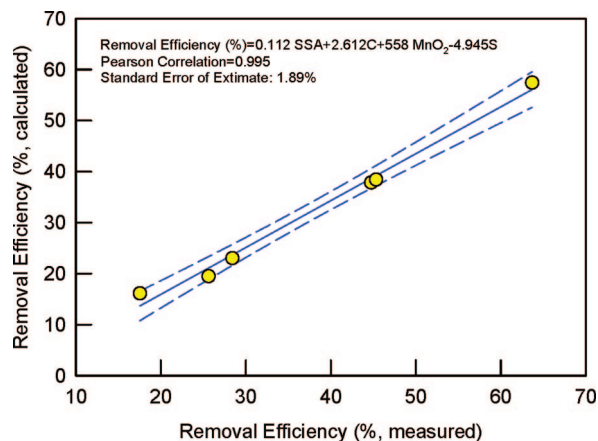
**Regression Models for Hg Removal by the ESP Unit.** According to the operational data provided by the facility, the particulate removal efficiency of the ESP unit is approximately 99%. Assuming 10% of the ash in the coal became bottom ash and an additional 2.5% of the ash was collected by a mechanical hopper for each coal burned, the removal efficiency of the mercury by the ESP and mechanical units for each coal tested can then be determined.

On the basis of the discussion provided above, the sulfur content in the coal, SSA of the fly ash, unburned carbon, and manganese content in fly ash are the parameters that were found to be significantly correlated with the adsorption of mercury on ESP ash. This conclusion is based on the regression results obtained by excluding coal sample #5. Therefore, a regression model representing the removal efficiency of Hg by the ESP unit can then be built upon the variable listed above.

$$\text{Hg}(\text{ESP}) = 0.112\text{SSA} + 2.612\text{C} + 558.33\text{MnO}_2 - 4.945\text{S}$$

A comparison between the removal efficiencies obtained from the regression model and actual measured results are shown in Figure 5. The Pearson correlation coefficients were calculated to be 0.995, and the standard error of the estimate was 1.9%. The regression results suggested that the models provide an excellent fit for the removal efficiency observed in this study, with the exception of coal sample #5.

It is a good interpretation of the currently activated carbon technique to control mercury emissions. The sorbent containing high carbon content with high SSA and good catalyst is efficient to convert gaseous mercury into particulate-bound mercury. Here, the high coefficient of manganese oxide indicates that



**Figure 5.** Comparison of calculated and measured Hg removal efficiency.

the chemical adsorption will be more important because the elemental mercury can be transformed during the adsorption.

## Conclusions

This study demonstrates the relative significance of coal and ash properties on the adsorption of Hg on fly ash. Unburned carbon, SSA, and manganese oxide content exhibited high positive correlations with the adsorption of Hg on ESP ash. The S content in coal showed the only negative effect observed in this study for the ESP fly ash.

In the case of MH ash, the adsorption of Hg was found to be correlated with unburned carbon and manganese oxide content. The relationships between the adsorption of MHP ash and ESP ash can be described by the following linear regression models:

$$\text{Hg}_{\text{ESP ash}}/\text{Hg}_{\text{coal}} = 0.348\text{C}_{\text{ESP}} - 0.04\text{SSA}_{\text{ESP}} + 98.143\text{MnO}_{2\text{ESP}} - 1.953\text{S}_{\text{ESP}}$$

$$\text{Hg}_{\text{MH ash}}/\text{Hg}_{\text{coal}} = 0.587\text{C}_{\text{MH}} + 0.284\text{MnO}_{2\text{MH}}$$

In addition to the Hg adsorption model, the removal efficiency of Hg by the ESP unit was successfully described by a statistical model. The observation can support the development of current sorbent techniques to reduce mercury emission from coal-fired power plants.

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