

# Factors Affecting Mercury Speciation in a 100-MW Coal-Fired Boiler with Low-NO<sub>x</sub> Burners

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The Western Kentucky University mobile laboratory for monitoring mercury emissions measured the mercury levels in a 100-MW boiler with wall-fired low-NO<sub>x</sub> burners. Mercury emissions were monitored while burning seven coals, using semicontinuous emission monitoring at the air preheater outlet and electrostatic precipitator outlet. The collected data was then scaled and analyzed using stepwise regression analysis. The results showed that initial mercury concentration in the coal, as well as chlorine and sulfur levels, all influence the amount of mercury emissions. After mercury content, chlorine had the major role in the levels of vapor-phase mercury present in the flue gas. Chlorine promotes the chemisorption of mercury onto fly ash. Sulfur was shown to be a major factor in the oxidation of elemental mercury but inhibited the adsorption of oxidized mercury onto the fly ash. Further experimental results suggest that both HCl and SO<sub>2</sub> may participate directly in the mercury oxidation mechanism.

## 1. Introduction

Because of the health risks posed by mercury, President Bush proposed “The Clear Skies Initiative”, which was introduced into the United States Congress as “The Clear Skies Act of 2004” (H. R. 999, S. 485). Under the legislation, mercury emissions will be cut by 69% by the year 2018—the first-ever national cap on mercury emissions. In addition, the law provides for emissions trading. The act allows for several means of verifying the mercury emissions from individual power plants. The mandated reduction in mercury emissions will have to be met by industry through the use of new pollution control technology, the use of existing technology, or a combination of the two.

One way of reducing mercury emissions is oxidizing elemental mercury to oxidized mercury. In flue gas, mercury exists in three primary forms: elemental mercury (Hg<sup>0</sup>), oxidized mercury, and particle-associated mercury. Most oxidized mercury in flue gas is in the mercury(II) state (Hg<sup>2+</sup>). Oxidized mercury is soluble and has a tendency to associate with particulate matter.<sup>1,2</sup> Therefore, emissions of oxidized mercury may be efficiently controlled by air emission and particulate-controlling equipment, such as a flue-gas desulfurization

(FGD) scrubber system, electrostatic precipitator (ESP), and activated carbon injection (ACI) systems.<sup>1,2</sup>

In contrast, elemental mercury is extremely volatile and insoluble. Elemental mercury has a high vapor pressure at the typical operating temperatures of air emissions equipment and particulate control devices (PCDs). Therefore, effective collection by particulate matter control devices is highly variable. Also, elemental mercury is not captured by FGD or PCD systems. Although some chemically treated activated carbons or selective absorbents may remove elemental mercury, they are more difficult to collect and treat. Therefore, elemental mercury emissions are harder to reduce than oxidized mercury emissions.<sup>3–7</sup>

Studies indicate that the distribution of mercury species in coal-fired flue gas is strongly dependent on

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the type of coal (e.g., bituminous, sub-bituminous, or lignite), the operating conditions of the combustion system (in terms of unburned carbon in the ash), and temperature and residence time in the particulate control device.<sup>2,7–14</sup> Several studies, including some conducted by the Mercury Emissions Monitoring Lab at Western Kentucky University (WKU), have shown a relationship between coal chlorine concentration and mercury oxidation.<sup>15</sup> Higher concentrations of ionic mercury are obtained in utility flue gas when the combusted coal has a high chlorine content (0.1–0.3 wt %).<sup>1,13,16–18</sup> Additional studies, including some conducted at WKU, have suggested that chlorine may have a role in mercury speciation.<sup>19,20</sup> As summarized in a recent review article by Pavlish et al., factors ranging from sulfur content to nitrogen content have been shown to influence mercury speciation.<sup>21</sup>

WKU recently had the unprecedented opportunity to use a commercially operating 100-MW boiler with wall-fired low-NO<sub>x</sub> burners for mercury emission studies.

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Unlike the Information Collection Request (ICR) of 1999 data from the U.S. Environmental Protection Agency (EPA), the data come from one combustor. In addition, two new sampling ports were made in the combustor, which allowed the team to test flue gas concentrations at locations other than just the stack. The semicontinuous coal emissions monitoring (SCEM) configuration was another unique feature of this study, which allowed two points to be tested simultaneously. Another significant feature of the research was the latitude to choose the coals used during the testing period. Therefore, the WKU team was able to test the effects of fuel composition in a non-laboratory-scale boiler without having to bias the results by changing boilers.

To take full advantage of this unique opportunity, WKU built a mobile mercury emissions monitoring laboratory (MMEML). The testing capabilities of the MMEML itself provided a unique testing opportunity. The MMEML has a SCEM system, P S Analytical's Sir Galahad, and two P S Analytical speciation/pretreatment units. WKU's SCEM setup allows for two points in a combustor to be monitored and speciated simultaneously, therefore reducing any bias introduced by changing SCEM systems or testing at different times.

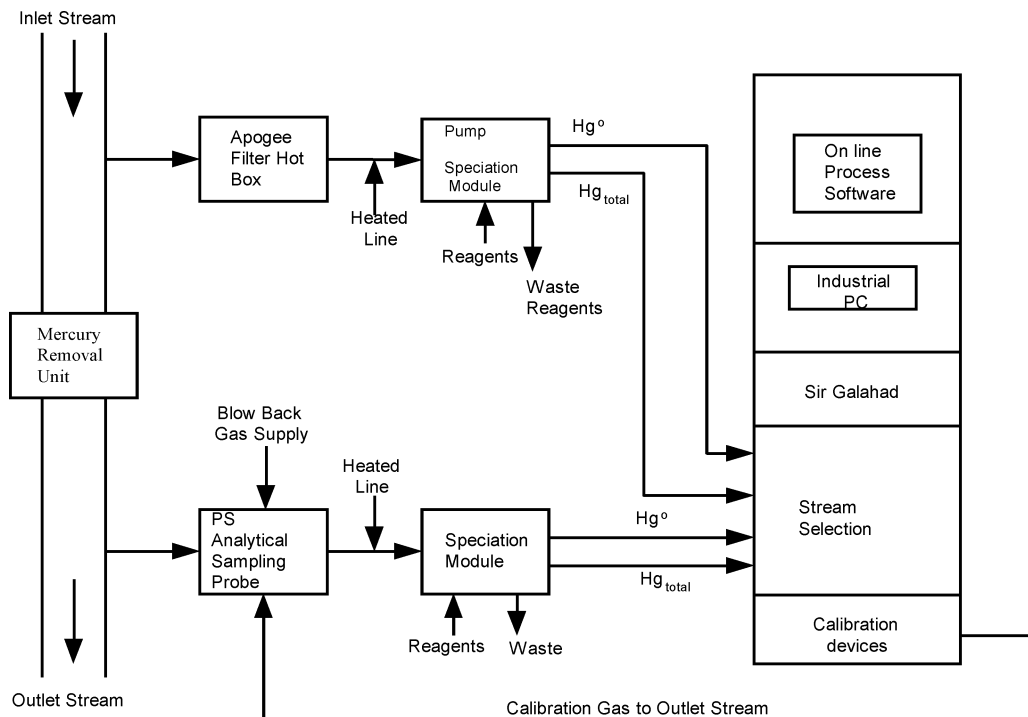
## 2. Experimental Section

**2.1. Semicontinuous Emissions Monitoring.** The semicontinuous emissions monitoring (SCEM) system used in this study is the P S Analytical Sir Galahad 10.525. It uses a gold trap to collect the mercury from the flue gas before analysis with an atomic fluorescence detector. The Sir Galahad system also has a mercury-vapor generator capable of supplying a constant stream of mercury vapor (~14 L/min) for calibration purposes. Another important feature of the Sir Galahad system is its stream selection box. The selection box allows the Sir Galahad software to differentiate between different streams for the measurement of different points or different mercury species.

Without the aid of a pretreatment system, the Sir Galahad is unable to speciate mercury. The pretreatment system splits the incoming flue gas into two streams. One stream passes through a potassium chloride (KCl) solution, which removes oxidized mercury and thereby allowing only elemental mercury to reach the detector. The other stream passes through a stannous chloride (SnCl<sub>2</sub>) solution, which reduces oxidized mercury to elemental mercury (Hg<sup>0</sup>), thus facilitating the measurement of total mercury. Both solutions also serve the dual purpose of removing acidic gases that could damage the gold detector.

The MMEML contains two pretreatment systems, which, along with the Sir Galahad stream selection box, allow for the monitoring and speciating of mercury at two locations simultaneously, using the same instrument. According to a search of the literature available at the time the experiment was designed, this was a new technique. The two locations tested were before and after the ESP. A diagram of the monitoring arrangement is shown in Figure 1. (All sample lines shown in the diagram are heated at 200 °C, to avoid the loss of mercury and the condensation of acidic gases.) In addition, the SCEM results were confirmed by the Ontario Hydro Method. The correlation between the two techniques has been published in a previous study.<sup>22</sup>

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**Figure 1.** Schematic configuration of the semicontinuous mercury emissions monitoring (SCEM) and pretreatment system.

**2.2. Testing Locations.** The results discussed in this paper were obtained at a 100-MW boiler with wall-fired low- $\text{NO}_x$  burners. The boiler is in a commercial plant and was operated normally throughout the duration of testing. The load carried by the plant was constant during the course of each individual test. A diagram of the boiler is shown in Figure 2. At the power station, the stack is a common stack for two units, and no sampling port is available at the common inlet of the stack. Therefore, the ESP outlet testing location provides data that best represents the total mercury processes that occur in the unit of interest (Unit 1) and provides the best opportunity to analyze the final results of the combustion process. Samples were also taken at the AP outlet. Seven coals were used during the course of the study and are described in Table 1.

**2.3. Gas Sampling.** Two instruments were used to analyze flue gas compositions. The photoacoustic multigas analyzer (INNOVA, model 1312), which uses an analysis method that is based on the absorption of infrared (IR) radiation, was used to measure the hydrogen chloride (HCl) and sulfur dioxide ( $\text{SO}_2$ ) concentrations in the flue gas. A Tempest 100 portable and flexible combustion emissions monitoring system was used to determine the  $\text{CO}_2$ ,  $\text{O}_2$ , and  $\text{NO}$  concentrations. These instruments are calibrated with standard gases twice each day. The measurement errors are as follows: 0.1 ppm for HCl; 1 ppm for  $\text{NO}$  and  $\text{SO}_2$ ; and 0.1% for  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ , and  $\text{O}_2$ . The results of the flue gas measurements are shown in Table 2. All flue-gas concentrations are the result of combustion processes and fuel content and have not been purposefully altered in any way.

### 3. Discussion

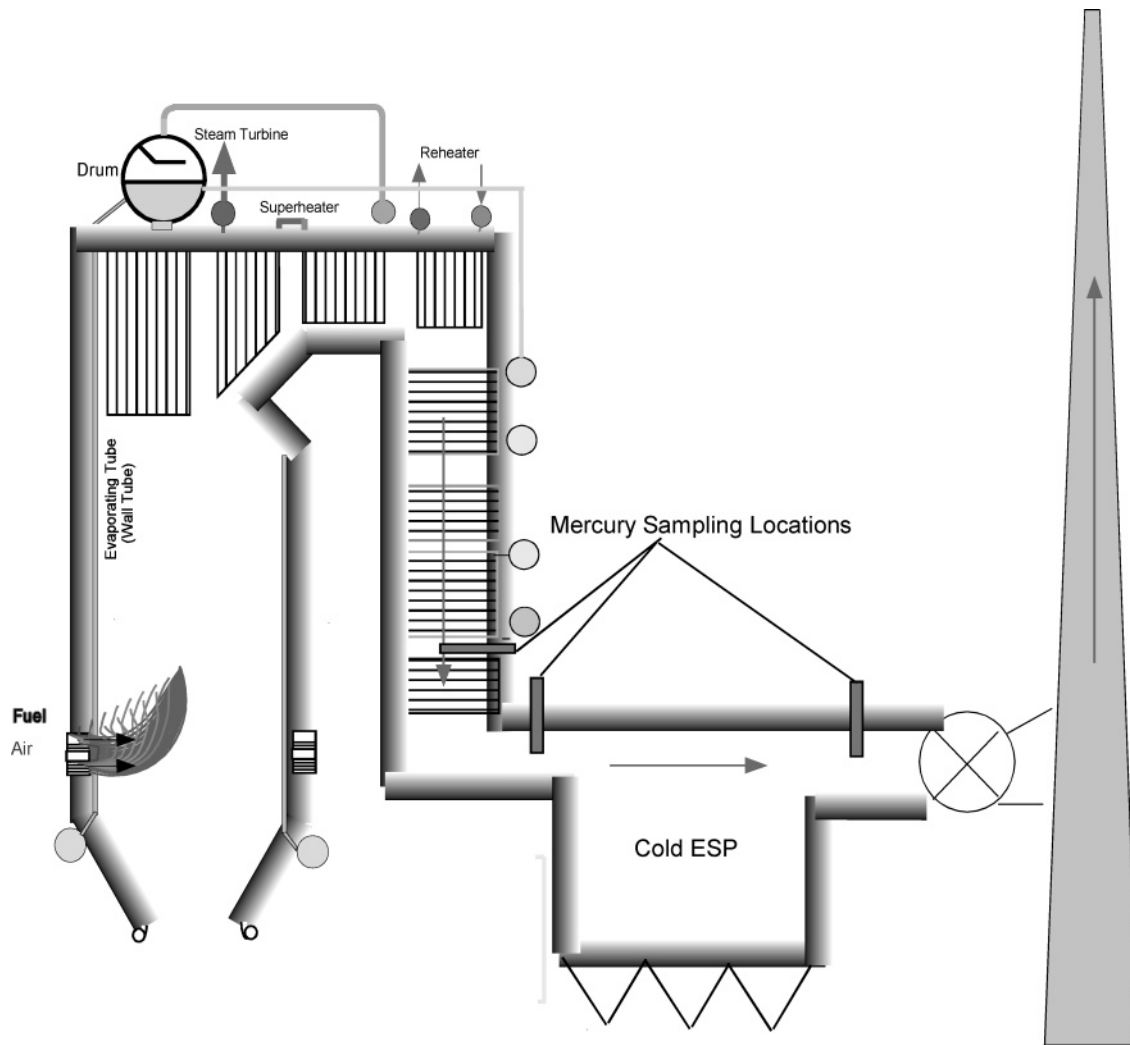
**3.1. Data Analysis.** Several studies have suggested many different factors that may influence mercury levels and its speciation. This study measured five different coal factors and five different flue gas factors for their effects on flue-gas mercury concentration and speciation. To correct for the different amounts of fuel mercury, coal mercury content was included as a factor in both the flue-gas and coal factor sets. The coal factor set and flue-gas factor set were then analyzed to

examine how they affected the dependent variables of total vapor-phase flue-gas mercury, elemental flue-gas mercury, and oxidized flue-gas mercury. Statistical analysis was used to compensate for tests where more than one variable changed and to allow the comparison of measurements taken at different locations on the same basis. To determine which factors most significantly affected mercury emissions, all measurements were standardized by scaling using eq 1:

$$\frac{\text{Measurement} - \text{Minimum Measurement}}{\text{Maximum Measurement} - \text{Minimum Measurement}} = \text{Scaled Value} \quad (1)$$

The standardized values were then subjected to stepwise regression with a probability of a Type I error to include or omit 0.15. Because there is covariance between several flue gas and coal factors, the measured characteristics were divided into coal characteristics and flue gas characteristics. The mercury concentration of the coal was a variable in both factor sets to correct for the different amounts of starting mercury. The testing location was also a variable in both factor sets, to correct for any bias in testing location. The characteristics groupings are shown in Table 3. The effects of measurement location were included in the analysis using the effect coding variable NAO. In total, 14 different data sets were used, one for each coal at each location. Each data set was the product of several 2-h testing periods taken over the course of at least 5 days. The standard deviations of the repetitive test results were within 10% for all samples during each individual coal run.

**3.2. Vapor-Phase Mercury.** Both coal and flue-gas factors performed well in describing the trends observed in the vapor-phase mercury data. The chosen coal factors were able to explain ~94% of the variance in vapor-phase mercury. The chosen flue-gas factors were able to describe ~95% of the variance. As observed in



**Figure 2.** Schematic diagram of the 100-MW boiler and mercury testing locations.

**Table 1. Analytical Values (Dry Basis) for Coals Used in This Study**

parameter	range
carbon content	68.89%–75.79%
nitrogen content	1.58%–1.77%
sulfur content	1.19%–2.04%
oxygen content	5.78%–8.03%
mercury content	0.06–0.24 ppm
chlorine content	908–3577 ppm

**Table 2. Range of Flue Gas Compositions at the Electrostatic Precipitator (ESP) Outlet**

factor	range
O <sub>2</sub> content	3.7%–7.1%
CO <sub>2</sub> content	11.9%–16.3%
NO content	221–384 ppm
SO <sub>2</sub> content	481–1328 ppm
HCl content	66–359 ppm

Table 4, several factors influence the vapor-phase mercury emissions, Hg(VP). Not unexpectedly, the major factor that affects mercury emissions is the concentration of mercury in the fuel coal. It was a highly significant factor, with the probability of affecting the total gaseous mercury being ~100% for both the coal and flue-gas factor sets.

In addition to the effects of coal mercury content, chlorine was also shown to have a major role in the level of gaseous mercury for both the coal and flue-gas data

**Table 3. Separation of Measured Variables into Coal and Flue Gas Factors**

coal factors	flue gas factors
coal chlorine content	HCl concentration in the flue gas
coal sulfur content	SO <sub>2</sub> concentration in the flue gas
coal nitrogen content	NO concentration in the flue gas
coal mercury content not the AP outlet = 0	O <sub>2</sub> concentration in the flue gas
	coal mercury content not the AP outlet = 0

**Table 4. Stepwise Analysis Results: Vapor-Phase Mercury**

factor	linear coefficient	P-value (probability of Type 1 error)
Coal Data Set, Intercept = -0.09852, R <sup>2</sup> = 93.61 <sup>a</sup>		
Hg	0.943	0.000
%S	0.158	0.043
Cl	-0.113	0.072
Flue-Gas Data Set, Intercept = -0.07829, R <sup>2</sup> = 95.27 <sup>a</sup>		
Hg	1.089	0.000
HCl	-0.129	0.048

<sup>a</sup> R<sup>2</sup> denotes the goodness of fit, adjusted for the degrees of freedom.

sets. An increase in the concentration of chlorine in the coal leads to a decrease in the level of gaseous mercury. An increase in the level of HCl in the flue gas also leads to a decrease in the level of gaseous mercury. The effects of both chlorine variables were very similar: the coal

**Table 5. Stepwise Analysis Results: Oxidized Mercury**

factor	linear coefficient	P-value (probability of Type 1 error)
Coal Data Set, Intercept = $-0.1117$ , $R^2 = 93.04^a$		
Hg	0.875	0.000
%S	0.246	0.008
Cl	$-0.109$	0.097
Flue-Gas Data Set, Intercept = $-0.1257$ , $R^2 = 91.1^a$		
Hg	0.92	0.000
SO <sub>2</sub>	0.163	0.132

<sup>a</sup>  $R^2$  denotes the goodness of fit, adjusted for the degrees of freedom.

chlorine content has a linear coefficient of  $-0.11$ , and the HCl concentration in the flue gas has a linear coefficient of  $-0.13$ , which suggests that the effects of coal chlorine content may be due to its co-linearity with the level of HCl in the flue gas.

The only difference between the two factor sets was that the coal sulfur content was shown to affect vapor-phase mercury but the SO<sub>2</sub> in the flue gas did not. These results are not necessarily contradictory. It could be that sulfur species other than SO<sub>2</sub> are responsible for the interactions with vapor-phase mercury. The effects of the SO<sub>2</sub> flue-gas content and coal sulfur content will be examined further later in this paper.

**3.3. Oxidized Mercury.** To provide further insight into mercury speciation, the levels of oxidized mercury in the flue gas (Hg<sup>2+</sup>) and elemental mercury in the flue gas (Hg<sup>0</sup>) were analyzed separately against the measured factors. The results for the coal factors explained 93% of the variance of Hg<sup>2+</sup>. The flue gas factors were able to account for 91% of the variance in Hg<sup>2+</sup>. Analysis showed the mercury content of the coal to be the major factor that affects Hg<sup>2+</sup> for both coal and flue-gas factors. (See Table 5.) The SCEM data showed a strong relationship between Hg<sup>2+</sup> and both the sulfur concentration of coal and the SO<sub>2</sub> concentration of the flue gas. An increase in either variable was related to an increase in oxidized mercury. As was seen with data analysis for total vapor-phase mercury, the sulfur concentration of the coal had a larger role than SO<sub>2</sub> in the flue gas.

In addition, the SCEM data indicated a significant relationship between the coal chlorine concentration and Hg<sup>2+</sup>. Surprisingly, an increase in the coal chlorine concentration caused a decrease in Hg<sup>2+</sup>, with a correlation coefficient of  $-0.11$ . This suggests that chlorine may promote the adsorption of Hg<sup>2+</sup> onto fly ash.

**3.4. Elemental Mercury.** As was the case with the Hg<sup>2+</sup> mercury species in the flue gas and the vapor-phase mercury data, coal mercury concentration was shown to be the major factor that affects the level of gaseous elemental mercury (Hg<sup>0</sup>). Coal mercury concentration produced similar changes in Hg<sup>0</sup> for both coal and flue-gas factor sets, with linear coefficients of 1.22 and 1.44, respectively. (See Table 6.) In addition to the effects of coal mercury concentration, both coal and flue-gas factor sets suggested that sulfur had a role in the level of Hg<sup>0</sup>. Both sets showed that Hg<sup>0</sup> decreased as the coal sulfur content or SO<sub>2</sub> in the flue gas increased. In contrast to the results for Hg<sup>2+</sup> in the flue gas, Hg<sup>0</sup> was more responsive to SO<sub>2</sub> levels in the flue gas than to the coal sulfur content. Only the flue-gas factor sets indicated that chlorine had a role in the level of Hg<sup>0</sup>. An increase in the amount of HCl in the flue gas was observed to cause a decrease in Hg<sup>0</sup>.

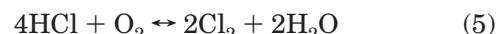
**Table 6. Stepwise Analysis Results: Elemental Mercury**

factor	linear coefficient	P-value (probability of Type 1 error)
Coal Data Set, Intercept = $0.05701$ , $R^2 = 66.86^a$		
Hg	1.22	0.001
%S	$-0.35$	0.074
Flue-Gas Data Set, Intercept = $0.14287$ , $R^2 = 77.69^a$		
Hg	1.44	0.001
SO <sub>2</sub>	$-0.49$	0.034
HCl	$-0.26$	0.112

<sup>a</sup>  $R^2$  denotes the goodness of fit, adjusted for the degrees of freedom.

**3.5. Mercury Transformations.** Disregarding the obvious importance of the initial mercury concentration of the coal, data analysis suggests that sulfur and chlorine have an important role in mercury transformations. The role of sulfur and chlorine, and their participation in the fate of mercury in flue gas, has long been a subject of research. Data from this study show an interesting trend: chlorine has a tendency to encourage the removal of mercury from the flue gas, regardless of speciation, whereas sulfur has a tendency to encourage the oxidation of flue-gas mercury, but not necessarily its removal from the flue gas.

Several studies performed on the laboratory scale, bench scale, and full scale have concluded that chlorine has a primary role in mercury oxidation.<sup>16,23–34</sup> Chlorine in coal is emitted at high temperatures, primarily as atomic chlorine, which then forms HCl or molecular Cl<sub>2</sub>, as shown in reactions 2–5.<sup>23,35</sup>



At the same time, elemental mercury from coal reacts

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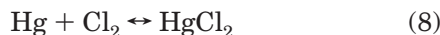
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with chlorine species to form oxidized mercury, as shown in reactions 6–9.



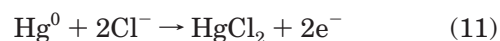
It is believed that the reaction illustrated by reaction 6 is the initial step of the mercury oxidation process, because of its fast rate. The slower reactions, represented by reactions 7 and 8, dominate the overall oxidation process.<sup>36</sup> Kinetic studies suggest that the quantity of  $\text{Cl}^-$  ions and their lifespan in the combustor are limiting factors in mercury oxidation.

There is a dispute as to whether HCl or  $\text{Cl}_2$  is the primary actor in mercury oxidation. Contributing to this argument is that, in the wet chemistry methods used to measure mercury speciation,  $\text{Cl}_2$  is more likely to be converted to HCl.<sup>24</sup> In a bench-scale study using simulated flue gas and the Ontario Hydro Method, Laudal and co-workers noted that the addition of  $\text{Cl}_2$  (10 ppm) decreased the amount of flue-gas elemental mercury by 31.49%, whereas the addition of HCl (50 ppm) only caused a 0.99% decrease.<sup>24</sup> However, in work that was conducted by Norton and co-workers, the addition of 50 ppm of HCl was determined to increase the percentage of feeding mercury in oxidized form by as much as 15%.<sup>25</sup> However, note that the Norton experiment was conducted in the presence of fly ash, compared to the absence of fly ash for the Laudal experiment.

In work by Galbreath and Zygarrlicke,<sup>29</sup> when the flue gas was spiked with 100 ppmv HCl, <35% of the input elemental mercury was recovered and only 80% of the input HCl was recovered, suggesting the formation of  $\text{HgCl}_2$  and its adsorption in the combustor. In addition, almost all of the reduction in gaseous mercury was a reduction in gaseous elemental mercury. The percentage of gas-phase mercury recovered as oxidized mercury remained fairly stable when spiking with elemental mercury or when spiking with elemental mercury and HCl. Because some of the HCl was converted to  $\text{Cl}_2$  (10% of the amount input), which form was responsible for the  $\text{HgCl}_2$  formation is unknown.<sup>29</sup>

Fujiwara and co-workers used a laboratory-scale coal-fired flame to investigate the effects of coal chlorine content and mercury emissions for five different coals. Their results showed that, although the relationship was not linear, there was an increase in mercury emission when the level of chlorine in the coal was increased dramatically from 2304 ppm for one coal compared to 176–406 ppm for the other four coals, and the percentage of oxidized mercury increased to 69%–

78%, compared to 2%–50% for the other coals.<sup>27</sup> A study by Slinger also noted that HCl oxidized up to ~75% of source mercury in a natural-gas-simulated flue-gas flame and that oxygen in the absence of HCl did not oxidize mercury by a detectable amount.<sup>31</sup> A study by the EERC, using a flow-through reactor, showed that the absorption of mercury on carbon-based sorbents was enhanced by the addition of HCl to the flue gas.<sup>37</sup> In addition, a study by Zeng, Jin, and Guo found that treatment of activated carbon with  $\text{ZnCl}_2$  increased the adsorption of  $\text{Hg}^0$ , compared to that of untreated activated carbon.<sup>38</sup> Furthermore, their results suggest that the mechanism of adsorption was chemisorption, rather than pure physisorption, because the impregnation of the activated carbon with  $\text{ZnCl}_2$  decreased the activated carbon's Brunauer–Emmett–Teller (BET) surface area and pore size. They suggested the mechanism shown in reactions 10–12:



Reaction 12 is of particular interest, because it suggests that, in an excess of chlorine, even oxidized mercury species can be chemisorbed directly through interaction with chlorine. This provides an explanation, other than pure mass action, for the decrease in both oxidized and vapor-phase mercury displayed in response to increased chlorine levels.

The data collected in the study reported in this paper offer support for chlorine having a role in both the chemisorption of mercury onto fly ash and mercury oxidation. The total amount of vapor-phase mercury was observed to decrease in response to increased coal chlorine content and increased HCl in the flue gas. However,  $\text{Hg}^{2+}$  was observed to decrease only in response to coal chlorine content, not the HCl content of the flue gas, suggesting that coal chlorine content has a role in the chemisorption of mercury. In contrast,  $\text{Hg}^0$  was observed to decrease in response to the HCl content of the flue gas, but not coal chlorine content, which suggests that HCl may be the active species in the oxidation of mercury, as shown in reaction 12 or reaction 5. If a different chlorine species covariant with HCl had a role in mercury oxidation, then the coal chlorine content should also affect the  $\text{Hg}^0$  levels.

A mechanistic explanation for why  $\text{Hg}^0$  levels seem to be unaffected by coal chlorine content has been proposed by Frandsen et al.,<sup>21</sup> who proposed that mercury oxidation can involve both sulfur and chlorine, via the mechanisms shown in reactions 13 and 14. If sulfur oxidizes mercury via this reaction, then the supply of chlorine would be continuously regenerated, instead of functioning as a limiting reagent. Therefore,  $\text{Hg}^0$  would not directly vary with chlorine levels, but rather with the concentration of HCl in the flue gas,

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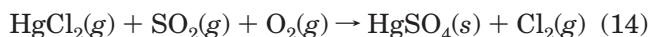
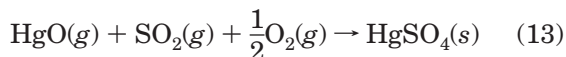
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assuming that HCl was the precursor of HgCl<sub>2</sub>. Instead, SO<sub>2</sub> levels would be an important factor in the degree of mercury oxidation and mask some of the effects of chlorine. In addition, the Frandsen model predicts that HgCl<sub>2</sub> will be the major oxidized species at temperatures of >700 K, with HgSO<sub>4</sub>(s) becoming the major species at temperatures of <590 K. Therefore, at the temperatures of this study, the balance of Hg<sup>2+</sup> would be transitioning from HgCl<sub>2</sub>(s) to HgSO<sub>4</sub>(s). As noted, the Frandsen model predicts HgSO<sub>4</sub>(s) to be the most stable form of mercury at temperatures less than 320 °C (~590 K), with its formation occurring via reaction 13, in the absence of chlorine, or via reaction 14, in the presence of chlorine.



The results of this study have shown that both the SO<sub>2</sub> concentration in the flue gas and coal sulfur content encouraged an increase in Hg<sup>2+</sup> and a decrease in Hg<sup>0</sup>, thereby supporting this explanation for the effects of both sulfur and chlorine. Thus, the results support chlorine encouraging the sorption of mercury onto fly ash and sulfur promoting mercury oxidation. The data also imply that HCl may have an active role in mercury oxidation.

Although the results of this study suggest that sulfur may encourage the oxidation of mercury, it seems to inhibit the chemisorption of mercury onto fly ash. It has been suggested that sulfur may promote the absorption of mercury by fly ash. In a surface study by Behra et al. of pyrite exposed to an aqueous mercury solution, ≡S–Hg–OH and ≡S–Hg–Cl complexes were detected.<sup>39</sup> However, work by Rio and Delebarre failed to find any Hg–S bonds in X-ray diffraction (XRD) examinations when an aqueous solution of mercury was filtered using fly ash.<sup>40</sup> Furthermore, sulfur is known to produce an acid gas that interferes with the trapping of mercury by activated carbon. In fact, H<sub>2</sub>SO<sub>4</sub>(g) has been shown to release previously trapped mercury. An explanation that explains both results was offered by Serre and Silcox. They proposed that SO<sub>2</sub> may compete with mercury for binding basic sites on the fly ash, but, under reducing conditions, or under conditions where a significant amount of sulfur was already present in the fly ash, it may serve as an oxidizing agent for Hg<sup>0</sup>.<sup>41</sup> The explanation by Serre and Silcox<sup>41</sup> would explain why the data from this study showed sulfur promoting mercury oxidation but causing increased levels of total mercury in the vapor phase. It would also explain why

the concentration of SO<sub>2</sub> in the flue gas, which participates directly in oxidation, had a greater effect on Hg<sup>0</sup> than the sulfur content of the coal, but a lesser effect on Hg<sup>2+</sup>, where the sulfur content of the coal would reflect both the oxidation of Hg<sup>0</sup> by SO<sub>2</sub> and the inhibition of the adsorption of Hg<sup>2+</sup> by other sulfur species.

This study suggests several possible avenues for further research. An expansion of the number of measurements would allow more factors to be tested simultaneously and further limit the possible effects of nonmechanistic co-linearity among variables. In addition, more testing locations would allow further elucidation, in regard to the effects of temperature, inorganic coal components, and fly ash concentration in the flue gas. Finally, further testing at other boilers would help to confirm the trends observed here.

#### 4. Conclusions

(1) The sulfur, chlorine, and mercury concentration of coals are all related to mercury emissions.

(2) Either the HCl in the flue gas or the coal chlorine content, or both, affected the levels of all mercury species in the flue gas.

(3) Chlorine promotes the chemisorption of mercury onto fly ash.

(4) HCl, or a chlorine species strongly covariant with it, seems to participate directly in the oxidation of mercury.

(5) Sulfur was shown to be a major factor in the oxidation of elemental mercury, but it actually inhibited the adsorption of mercury onto fly ash.

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