

# Impact of Coal Chlorine on Mercury Speciation and Emission from a 100-MW Utility Boiler with Cold-Side Electrostatic Precipitators and Low-NO<sub>x</sub> Burners

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Field tests on mercury speciation and emission while burning Kentucky and Illinois coals with different chlorine contents were performed in a 100-MWe pulverized-coal boiler with low-NO<sub>x</sub> burners. Seven coals were used during the tests and were grouped into two sets for comparison, with the baseline coal being shared between the two sets. The first set of four coals was used to investigate the effect of chlorine in coal on mercury emission and its speciation by selecting coals with similar mercury contents and different chlorine contents. The four coals in the second set were selected to investigate the effect of mercury contents in coal on mercury emission and its speciation by choosing coals with similar chlorine contents and different mercury contents. The mercury concentration and speciation in the flue gas were determined using the American Society for Testing and Materials (ASTM) standard Ontario Hydro Method (OHM) and a PS Analytical Semi-continuous Emissions Monitoring (SCEM) system. Flue gas samplings were performed at two locations: upstream before the electrostatic precipitator (ESP) inlet and downstream after the ESP outlet. A thorough comparison between the two monitoring methods was made. A sampling bias was found in the OHM sampling performed at the ESP inlet, because of the accumulation of ash with a high carbon content on the OHM filter. An ash-free sampling probe should be used with the OHM impinger train for obtaining accurate mercury information whenever ash concentrations are high. Mercury emission and speciation for the seven test coals at the ESP outlet location are described and discussed. Results indicate that the coal chlorine content has an impact on the mercury oxidation processes, which are mitigated by high concentrations of SO<sub>2</sub>. It is speculated that SO<sub>2</sub> limits Cl<sub>2</sub> formation.

## 1. Introduction

In 1997, the United States Environmental Protection Agency (EPA) issued a mercury study report to the U.S. Congress, which estimated that anthropogenic sources in the United States emitted 158 tons of mercury into the atmosphere in 1994–1995, with coal-fired combustion sources accounting for 48 tons of that total.<sup>1–3</sup> Because of the danger to human health posed by mercury, Congress and the EPA are determined to regulate mercury emissions. Three important target

dates have been incorporated into EPA's plan to regulate mercury emissions from coal-fired electric generating units: the proposal of regulations by December 2003, the promulgation of regulations by December 2004, and, finally, compliance with the regulations by December 2007.<sup>4</sup> EPA seeks to reduce the total mercury emissions in 2010 and again in 2018.<sup>4</sup>

Mercury in the flue gas is classified as particle-bound mercury and gaseous mercury existing as either oxidized mercury or elemental mercury. The particle-bound mercury can be easily captured by ash collection apparatuses, such as mechanical hoppers, electrostatic precipitators (ESPs), and baghouses. The capture of gaseous mercury by flue gas particles is dependent on several factors that affects the mercury removal ef-

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efficiency of ash collection devices downstream in the flue gas duct. Oxidized mercury is water-soluble and has a tendency to associate with particulate matter, allowing it to be controlled, along with ash and SO<sub>2</sub>, in existing air pollution control devices (APCDs) such as ESPs and wet-flue gas desulfurization (wet-FGD) scrubbers.<sup>5–9</sup> Elements found in coal, such as sulfur and chlorine, will sometimes inhibit or promote mercury emissions. Studies using small-scale facilities have shown that coals with high chlorine contents could achieve as much as 99% conversion of the elemental mercury to oxidized mercury.<sup>10–12</sup> Elemental mercury is insoluble in water and extremely volatile at the operating temperatures of APCDs. It can also remain suspended in the air and be transported a long distance from its emission source.

Mercury in coal will be emitted into the flue gas as elemental mercury at higher temperatures in the coal combustion process. Thermodynamic equilibrium calculations predict that all gaseous mercury in a coal combustion flue gas will exist as mercuric chloride (HgCl<sub>2</sub>) at temperatures of <450 °C.<sup>13</sup> However, actual mercury speciation data collected by the EPA's Information Collection Request (ICR) database showed that, even at the lower temperatures of APCDs, a small amount of elemental mercury still exists in the flue gas. The difference between thermodynamic calculations and the actual behavior of mercury in combustion processes implies that thermodynamic equilibrium has not been reached. Temperature and flue gas species, such as SO<sub>x</sub>, NO<sub>x</sub>, HCl, and Cl<sub>2</sub> downstream of the flue gas duct, have strong influences on mercury speciation and abatement.<sup>14–16</sup> Recent studies indicate that the distribution of mercury species in coal-fired flue gases is strongly

dependent on the type of coal (e.g., bituminous, sub-bituminous, or lignite), because of the different sulfur and chlorine contents in coal, as well as the APCD configuration.<sup>17</sup> A detailed analysis of the mercury oxidation processes will be addressed in this paper.

In an interim report<sup>17</sup> issued by EPA, it was stated that a total of 23 coal-burning units with wet-FGD scrubbers have been tested thus far. Among them, seven units also used particulate matter (PM) scrubber systems to control particulate emissions, eight units used cold-side ESPs, six units used hot-side ESPs, and two units used fabric filters (FFs). The results of emission tests on wet-FGD systems indicated that the best levels of total mercury capture were exhibited by units burning bituminous coals that are equipped with FFs (98%), cold-side ESPs (75%), or hot-side ESPs (50%). ICR data also indicated that mercury<sup>17,18</sup> removals across all cold-side ESPs averaged 27%, compared to 4% for hot-side ESPs. Removals for FFs were higher, averaging 58%, which was attributed to additional gas–solid contact time for oxidation. The higher capture levels for bituminous coal-fired boilers equipped with cold-side ESPs, hot-side ESPs, or FF control devices are consistent with the high levels of elemental mercury oxidation associated with these coal-boiler control classes. The very high levels of mercury capture exhibited by the bituminous coal-fired boiler units with a FF and wet-FGD system can be attributed to high levels of elemental mercury oxidation and to the capture of particle-bound mercury and oxidized mercury as the flue gas passes through the FF cake.

After reviewing the Part III stack data in the ICR database, the Electric Power Research Institute (EPRI) concluded that the chlorine concentration in the coal was the most important variable influencing mercury speciation and removal.<sup>15</sup> Further statistical tests by EPRI demonstrated that the EPA selection approach had a tendency to under-represent some popular categories of coal ranks and APCDs. For example, the category of bituminous coal, no scrubbers, and cold-side ESP represents almost 40% of all the units and >50% of all the fuel mercury introduced into coal-burning power plants. However, only three sites were tested in this category. The chlorine contents in the coals studied in the ICR was always <1000 ppm. The coals selected for the current study had a wide range of chlorine contents and other constituents. Consequently, the results of this study could be a good addition to the EPA ICR database for investigation of mercury speciation behavior.

Part of the background research for the present study was conducted using a 0.1-MWe fluidized bed combustion (FBC) system at Western Kentucky University (WKU).<sup>19,20</sup> When high chlorine (0.30%–0.50% chlorine) coals were burned in this system, ~70% of the total mercury in the fuel was absorbed by the fly ash, with the remaining 30% emitted in the flue gas. Of the emitted mercury, ~98% existed in an oxidized form, which can be easily captured by air emission and

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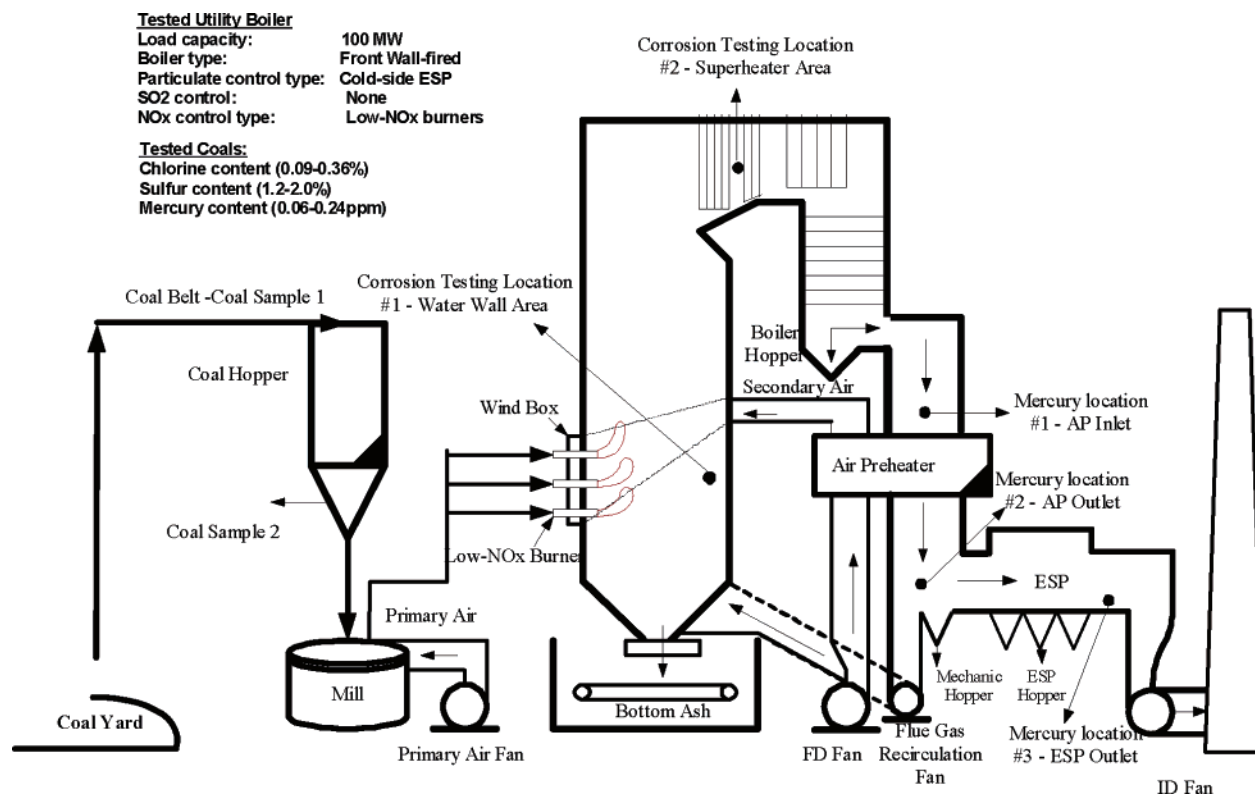
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**Figure 1.** Schematic diagram of the 100-MWe pulverized coal utility boiler and mercury testing locations.

particulate-control apparatuses. In a collaborative effort between WKU, EPRI, the Illinois Clean Coal Institute (ICCI), and a power station, a program for firing coals with high chlorine contents to study mercury emissions was initiated. Seven coals with different mercury and chlorine contents were used for the tests. The Ontario Hydro Method (OHM) and semi-continuous emission monitoring (SCEMs) were used to monitor mercury emissions and speciation.

## 2. Experimental Section

**Test Unit.** The configuration and characteristics of the test unit are as follows: load capacity, 100 MW; boiler type, front wall-fired; particulate control, cold-side ESP; SO<sub>2</sub> control, none; and NO<sub>x</sub> control, low-NO<sub>x</sub> burners.

**Test Locations.** The tests were performed during the normal operation of the 100-MW boiler system, and the load was constant during the course of each individual test. A schematic diagram of the test boiler is shown in Figure 1. The concentration of mercury in the flue gas was measured at two locations. Location 1 was before the mechanical dust collector and ESP, and Location 2 was after the ESP in the duct leading to the stack. The power station stack is shared by two boiler units; therefore, the ESP outlet test location was selected to provide data that best-represented the total mercury processes that occur in the unit of interest (Unit 1). Both locations were sampled using the OHM and SCEM methods. A common sampling port at the air preheater (APH) outlet was used for both OHM and SCEM sampling. At the ESP outlet, there were two sampling ports: one for OHM sampling activity and another for SCEM sampling activity.

Neither of the locations met the requirements of EPA Method 1.<sup>21</sup> However, it was expected that the mercury would primarily exist in the gas phase at both of the sampling locations. The small variations in oxygen concentration and ash content measured at the sampling locations indicated gas-phase uniformity.

**Fuels Tested.** Seven coals with different mercury, chlorine, and sulfur levels were tested. The ranges of mercury, chlorine, and sulfur concentrations were 0.06–0.24 ppm, 0.09%–0.36%, and 1.2%–2.0%, respectively. Analytical data collected with instrumentation from the LECO Corporation (St. Joseph, MI) are given in Table 1. Test methods followed included ASTM standard methods D5142 (for moisture, ash, and volatile matter), D5373 (for carbon, hydrogen, and nitrogen content), D4239 (for sulfur content), D4208 (for chlorine content), D3761 (for fluorine content), D6722 (for mercury content), and D5865 (for heating value).<sup>22</sup> The compositions of ashes prepared from the seven coal samples are shown in Table 2. A Rigaku energy-dispersive X-ray fluorescence (XRF) spectrometer was used for the analysis of the ashes, following ASTM Method D4326.<sup>22</sup> It has been reported that the oxides CaO, Fe<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, and V<sub>2</sub>O<sub>5</sub> may affect mercury transformation.<sup>17</sup> Only Fe<sub>2</sub>O<sub>3</sub> was observed to vary significantly between samples. Analytical data for the fly ashes taken from the mechanical hoppers and ESP hoppers are shown in Table 3. The loss on ignition (LOI), as well as carbon and sulfur contents in the ash samples, were determined using ASTM Methods D5142, D5373, and D5016, respectively.<sup>22</sup> It was found that the LOI determined for fly ash was dependent on the coal properties and behavior of the low-NO<sub>x</sub> burner. The burner and fuel/air distribution parameters for the low-NO<sub>x</sub> burners were kept the same for all seven coals. Only small portions of sulfur and chlorine were captured

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**Table 1. Analytical Data for the Seven Coals Used in the Study, Reported on a Dry Basis**

parameter	coal 1	coal 2	coal 3	coal 4	coal 5	coal 6	coal 7
Proximate Analysis							
moisture, after air-drying (wt %)	2.63	2.60	2.76	3.73	7.73	4.69	3.25
ash (wt %)	9.60	9.89	9.63	8.61	10.93	8.37	16.20
volatile matter (wt %)	32.89	32.86	35.89	36.39	38.57	37.81	36.12
fixed carbon (wt %)	54.88	54.64	52.72	51.27	45.68	53.83	45.68
Ultimate Analysis							
C (wt %)	75.79	75.84	74.81	75.18	75.18	76.58	68.89
H (wt %)	5.00	5.04	4.83	4.88	4.47	5.64	4.81
N (wt %)	1.77	1.66	1.58	1.67	1.42	1.66	1.58
S (wt %)	1.30	1.78	1.20	1.19	1.42	1.41	2.04
O (wt %)	6.54	5.78	7.95	8.03	6.58	6.34	6.48
Miscellaneous Analysis							
Hg (ppm, wt)	0.12	0.10	0.11	0.13	0.06	0.12	0.24
F (ppm, wt)	115	31	48	85	97	92	
Cl (ppm, wt)	1006	1449	908	1348	1171	3577	1536
high heating value, HHV (Btu/lb)	13309	13257	13196	13544	13783	13530	12459

**Table 2. Elemental Oxide Compositions of Ashes Prepared from Coals Used in the Study**

oxide	coal 1	coal 2	coal 3	coal 4	coal 5	coal 6	coal 7
Na <sub>2</sub> O (%)	0.47	0.37	0.45	0.33	1.07	1.11	0.33
MgO (%)	1.00	1.12	1.07	1.17	1.10	0.71	1.12
Al <sub>2</sub> O <sub>3</sub> (%)	25.11	26.05	26.71	22.82	21.57	23.31	24.24
SiO <sub>2</sub> (%)	50.59	50.43	52.69	50.11	49.53	49.42	47.47
CaO (%)	1.45	0.97	1.51	2.85	2.18	1.94	1.08
K <sub>2</sub> O (%)	1.86	2.69	2.18	2.26	2.59	2.83	3.55
SO <sub>3</sub> (%)	1.24	1.04	1.41	2.24	1.39	1.32	0.77
P <sub>2</sub> O <sub>5</sub> (%)	0.24	0.21	0.30	0.17	0.43	0.36	0.22
BaO (%)	0.20	0.20	0.26	0.20	0.00	0.06	0.09
SrO (%)	0.11	0.11	0.20	0.09	0.08	0.09	0.07
Fe <sub>2</sub> O <sub>3</sub> (%)	12.38	15.25	8.82	12.23	14.56	14.95	17.68
MnO <sub>2</sub> (ppm)	165	147	162	466	245	230	280
TiO <sub>2</sub> (%)	1.43	1.17	1.49	1.13	1.24	1.36	1.17
V <sub>2</sub> O <sub>5</sub> (ppm)	261	318	269	236	289		

**Table 3. Analytical Data for Fly Ashes Taken from the Mechanical and Electrostatic Precipitation (ESP) Hoppers**

sample	C (wt %)	LOI <sup>a</sup> (wt %)	S (wt %)	Cl (wt %)	F (wt ppm)	Hg (wt ppm)
Ash Collected from the Mechanical Hopper						
coal 1	5.21	5.5	0.11	130	50	0.09
coal 2	4.07	4.08	0.11	100	36	0.06
coal 3	7.80	8.40	0.25	79	57	0.11
coal 4	9.52	11.69	0.20	141	262	0.23
coal 5	6.79	6.84	0.11	169	28	0.12
coal 6	5.60	6.76	0.18	510	83	0.11
coal 7	2.06	3.07	0.1	189		0.09
Ash Collected from the ESP Hopper						
coal 1	4.91	5.84	0.62	107	195	0.41
coal 2	3.9	5.17	0.63	127	610	0.3
coal 3	5.3	6.51	0.47	132	149	0.59
coal 4	6.57	7.56	0.57	222	303	1.11
coal 5	6.89	7.72	0.41	221	107	0.99
coal 6	3.9	5.12	0.67	530	181	0.67
coal 7	2.41	3.44	0.59	200		0.3

<sup>a</sup> Loss on ignition.

by fly ash in the duct. Over 90% of the sulfur and chlorine in the coal remained in the gas phase.

**Sampling and Analysis Techniques.** The EPA OHM procedure and EPA Isokinetic Sampling Method 17 (in-stack filtration) were followed, according to the temperature and configuration of the sampling ports. The recovery solutions were digested and analyzed using the Hydra Prep mercury solution digestion equipment and the Hydra AA mercury solution analyzer from the Leeman Instrument Company. This mercury analyzer is an automated unit that uses a dual-beam, cold vapor atomic absorption spectrometry (AAS) system. This system has a detection limit of 1 part per trillion (ppt) mercury. Another mercury analysis system used was the SCSEM system

from PS Analytical. This system uses a gold trap to collect the mercury from the flue gas before analysis with an atomic fluorescence detector. Without the aid of a pretreatment system, the atomic fluorescence detector is not protected from acidic flue gas and is also unable to determine mercury speciation. The pretreatment system splits the incoming flue gas into two streams. One stream passes through a potassium chloride (KCl) solution, which removes oxidized mercury; thereby allowing only elemental mercury to reach the detector. The other stream passes through a stannous (SnCl<sub>2</sub>) chloride solution, which reduces oxidized mercury to elemental mercury, thus facilitating the measurement of total mercury. Both solutions also serve the dual purpose of removing acidic gases that could damage the gold detector.

**Ontario Hydro Method (OHM).** OHM is the only EPA method for measuring and speciating mercury in flue gas that has been approved by ASTM (Method D6784).<sup>23</sup> Laboratory and field validations have indicated relative standard deviations of typically 10%, far better than the minimum criteria set by EPA Method 301.<sup>24–26</sup> Depending on the flue gas temperature, the OHM has two possible configurations, based either on EPA Method 5 (out-of-stack filtration)<sup>27</sup> or EPA Method 17 (in-stack filtration).<sup>28</sup>

At the test site, the EPA Method 17 configuration was used at the sampling point after the ESP. Because of the high volume of fly ash immediately before the ESP region, a modified sampling train (EPA Method 5), with both in-stack and out-of-stack filtration, was used. The standard OHM consists of three key elements: isokinetic sampling, recovery, and solution analysis. All activities followed EPA quality assurance/quality control (QA/QC) procedures. Because of a fly ash bias discovered during the course of this work with the OHM, an ash-free probe was used to replace the traditional OHM probe for the combustion of three coals: coal 3, coal 5, and coal 6. The ash-free flue gas sampling probe (from Apogee Scientific, Ltd.) was designed from the inertial de-dust prin-

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ciple. The ash-free sampling probe allowed no ash coke to form in the path of the sampled flue gas; thus, the effect of ash coke on mercury concentration and its speciation was eliminated.

Using the OHM, three forms of mercury are measured: (1) particle-bound mercury, separated by filtration; (2) gaseous oxidized mercury, collected in KCl impingers, and (3) gaseous elemental mercury that is oxidized in the collection solutions of nitric acid/peroxide and acidified permanganate. Early indications of a low bias in elemental mercury measurements with high levels of SO<sub>2</sub> in the flue gas were corrected by adding an impinger that contained nitric acid/hydrogen peroxide before the acidified permanganate solutions, to avoid a possible reduction reaction. Another concern was the possible presence of Hg<sup>+</sup> species in the flue gas, which would be captured in KCl impingers and converted to Hg<sup>2+</sup> in acidified permanganate solutions during the subsequent solution recovery process. The Hg<sup>+</sup> species gives the same results as Hg<sup>2+</sup> and is, therefore, counted as oxidized mercury or Hg<sup>2+</sup>. However, it is generally assumed that all forms of oxidized mercury in the hot flue gas occur as Hg<sup>2+</sup>. This is a reasonable assumption, because Hg<sub>2</sub>-Cl<sub>2</sub> is not thermodynamically stable in the flue gas and disproportionates rapidly to produce Hg<sup>0</sup> and Hg<sup>2+</sup>.<sup>29,30</sup>

The versatile Apex Instruments isokinetic sampling train (probe with glass liner, quartz filter or heated filter box, Method 5 glassware set, U-cord, brushes, and metering console) was used. A sampling time of ~2 h was required to collect gas samples with a volume of 1–1.5 sccm (standard cubic meters). After sampling, solutions were digested and analyzed using the Leeman Hydra Prep digestion equipment and the Leeman Hydra AAS analyzer, respectively.

**PS Analytical Semi-continuous Emission Monitoring (SCEM) System.** The PS Analytical SCEM system consists of five major components:

- (1) A probe, filter, and pump module.
- (2) Heated Teflon sample lines, which are normally maintained at 200 °C and are needed to prevent mercury losses along the sample lines, maintain the speciation that is in the stack, and reduce condensation of acidic gases.
- (3) A mercury conversion system.
- (4) An analyzer and data collection system.
- (5) The system also has a mercury vapor generator. This device is able to supply a constant stream of mercury vapor and blank at typically 14 L/min. These gases pass through the valve-switching box and can be directed to the probe to check the system bias completely.

**LECO AMA-254 Advanced Mercury Analyzer.** Fly ashes collected from the OHM standard filter, mechanical hoppers, and ESP hoppers were analyzed with the LECO AMA-254 analyzer. This direct combustion mercury analyzer was the principal instrument used to develop the newest ASTM standard method of analysis for mercury in coal and combustion residues (Method D6722).<sup>22</sup> The AMA-254 analyzer has a 0.01-ng mercury detection limit, a working range of 0.05–600 ng, a reproducibility of <1.5%, and a 5-min analysis time.

**Flue Gas Analyzers.** Three flue gas analyzers were used in this study, to obtain accurate concentrations of different flue gas compositions and validate concentrations of flue gas compositions through replication among different measurement methods. The capabilities of the three gas analyzers provided duplicate or triplicate determinations for several gases, such as SO<sub>2</sub> and NO, and showed a numerical agreement of <5% difference, so that gas measurements could be validated.

A photoacoustic multigas analyzer (INNOVA model 1312) that uses an analysis method based on the absorption of IR

radiation, was used to measure the carbon dioxide (CO<sub>2</sub>), moisture (H<sub>2</sub>O), hydrogen chloride (HCl), nitrous oxide (N<sub>2</sub>O), and ammonia (NH<sub>3</sub>) concentrations in the flue gas. A dilution system was coupled with the analyzer to protect sensor cases from corrosion and breakage. An IMR 7000 multigas analyzer, which uses an analysis method based on an electrochemical principal of measurement, was used to determine carbon monoxide (<2000 ppm), oxygen (O<sub>2</sub>), sulfur dioxide (SO<sub>2</sub>), and nitric oxide (NO) concentrations. A portable and flexible Tempest 100 combustion emissions monitoring system also was used, to determine the H<sub>2</sub>S (<1000 ppm), CO (1%–10%), O<sub>2</sub>, NO, and SO<sub>2</sub> concentrations.

### 3. Results and Discussion

#### Temperature and HCl Profiles in the Test Boiler.

Independent of the species of mercury in coal, mercury is emitted from coal in the most thermodynamically stable species—elemental mercury—when the temperature is >750 °C.<sup>14</sup> As the flue gas cools, the mercury oxidation reactions will reach equilibrium under typical flue gas compositions, allowing the formation of oxidized mercury. SO<sub>2</sub>, NO<sub>x</sub>, HCl, and Cl<sub>2</sub> are the main constituents in the flue gas that affect the mercury chemistry. The temperature profiles and gas compositions across the depth and height of the Unit 1 boiler were determined. Downstream of the boiler, the temperatures at the air preheater (APH) inlet, ESP inlet, and ESP outlet were 700 °F (365 °C), 310 °F (155 °C), and 310 °F (155 °C), respectively. The concentration of SO<sub>2</sub> was ~800 ppm. A typical gas composition profile for HCl is shown in Figure 2 as a typical coal for this unit was burned. The Cl<sub>2</sub> profile could not be obtained, because of the detection limitations of the instrument.

**Gas Composition Analysis.** Mercury speciation in low-temperature regions is dependent on the flue gas atmosphere, which varies with fuel composition, combustion process conditions, and the type of pollution control devices used. As indicated previously, SO<sub>2</sub>, NO<sub>x</sub>, HCl, and Cl<sub>2</sub> were determined to be the main flue gas components that affect mercury speciation. Three commercial gas analyzers were used to measure these gases.

The compositions of the flue gases from burning the seven test coals, as measured at the ESP outlet, are given in Table 4. The oxygen concentrations at the different mercury sampling locations varied along the ducts, with the highest oxygen concentration being found at the ESP outlet. NO was the main nitrogen species found in the flue gas and was almost constant, at ~300 ppm, for the different test coals. The HCl concentrations measured in the flue gas for coal 1 (0.10% Cl) were in the range of 80–96 ppm. HCl concentrations were <100 ppm for coal 2 (0.15% Cl), coal 3 (0.091% Cl), and coal 5 (0.12% Cl). A HCl concentration of ~150 ppm HCl was detected in the flue gas for coal 7, and a HCl concentration of 300 ppm was observed in the flue gas for coal 6. Variations of HCl and SO<sub>2</sub> in the flue gases generally correlated to the chlorine and sulfur contents in the coals burned. Although a portion of the HCl was captured by the fly ash, the majority of HCl and SO<sub>2</sub> remained in the gas phase.

**Mercury Speciation and Emission.** Gaseous elemental mercury is primarily emitted from coal in the high-temperature zone during the combustion process. As it travels downstream in the duct, some of it undergoes an oxidizing reaction and is captured on

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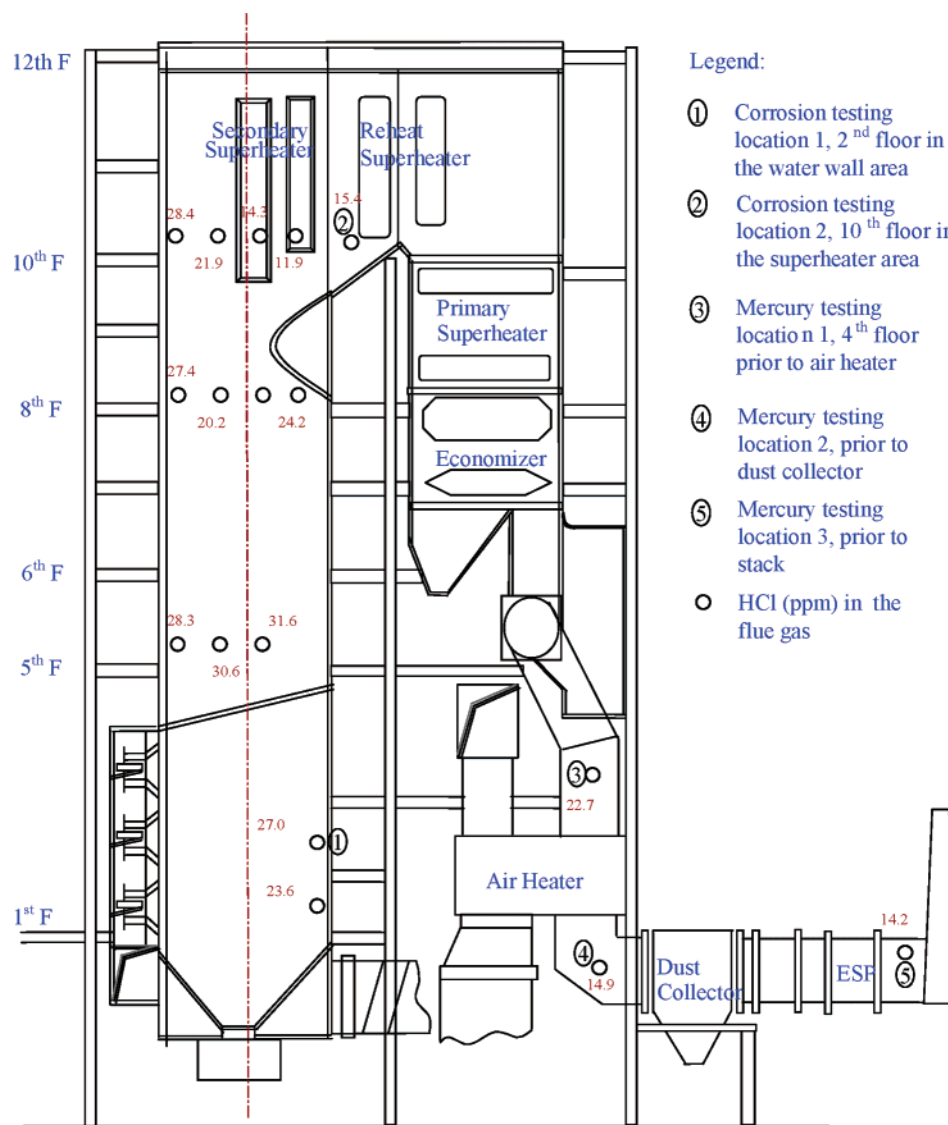


Figure 2. HCl composition profile inside the 100-MWe boiler.

Table 4. Average Flue Gas Compositions at the ESP Outlet Location for All Test Coals

sample	O <sub>2</sub> (%)	CO <sub>2</sub> (%)	SO <sub>2</sub> (ppm)	NO (ppm)	HCl (ppm)
coal 1	6.66	11.91	731.1	203.8	79.9
coal 2	6.72	11.43	892.2	290.2	84.8
coal 3	6.32	13.12	683.7	220.2	71.7
coal 4	6.66	12.34	575.4	327.8	108.7
coal 5	7.29	11.13	569	275.5	66.3
coal 6	6.21	12.71	725.5	269.1	298.1
coal 7	6.38	13.7	1164.9	281.9	137.3

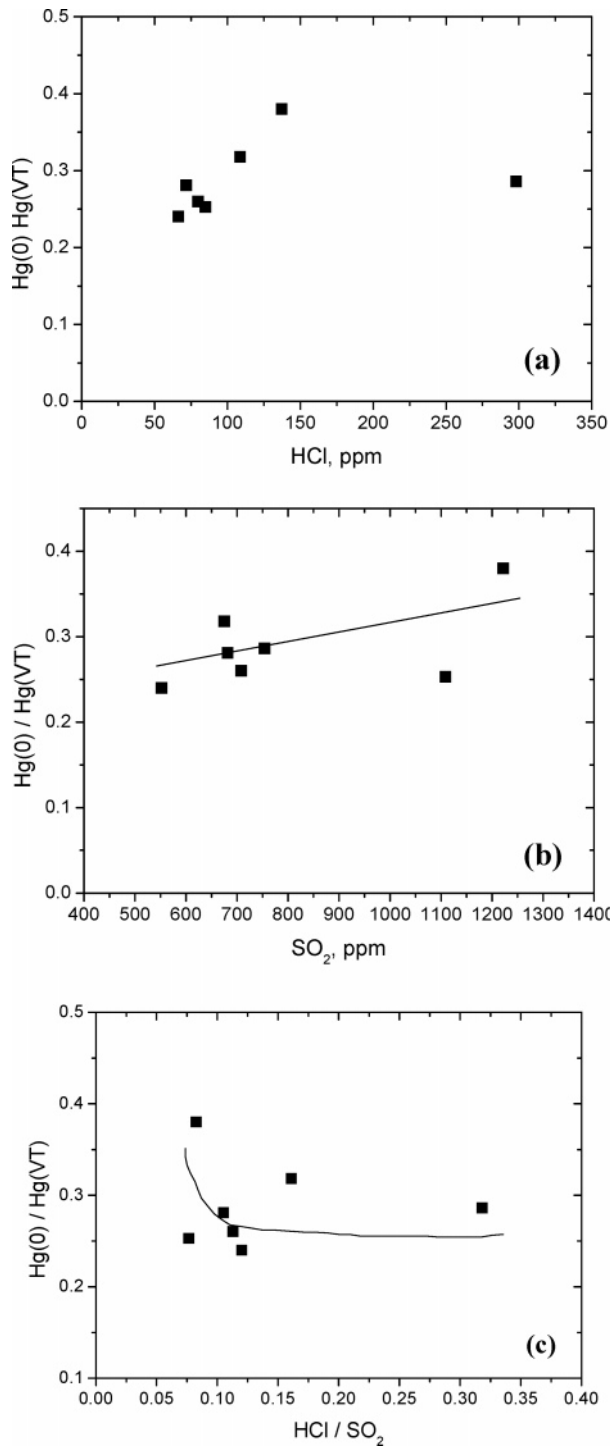
particles. The extent to which oxidation or capture occurs is a function of temperature, flue gas composition, and fly ash composition. Understanding how these factors affect mercury transformations in the flue gas is important in controlling mercury emissions, because oxidized mercury and particle-bound mercury are more easily controlled by the presently available APCDs.

All data were corrected to a 3% oxygen basis in the flue gas, to compare mercury concentrations. A minimum of two samples was collected for each coal at each location. The standard deviations of the repetitive test results were within 10% for all samples during each individual coal run.

**Ontario Hydro Method Data.** Plots of the OHM mercury test results versus the concentrations of key

flue gas components at the ESP outlet are shown in Figure 3. In this figure, mercury speciation is defined as the percentage of gaseous elemental mercury to the total gaseous mercury ( $\text{Hg}(0)/\text{Hg}(\text{VT})$ ). The figure includes the following: gaseous mercury speciation versus HCl concentration in the flue gas (Figure 3a), gaseous mercury speciation versus SO<sub>2</sub> concentration in the flue gas (Figure 3b), and gaseous mercury speciation versus the mole ratio of hydrogen chloride to sulfur dioxide in the flue gas (Figure 3c).

Direct correlation of mercury speciation in the flue gas with the chlorine and sulfur contents in coal and ash will help evaluate the effect of coal type on mercury speciation. As mentioned previously, a mercury interim report indicated that mercury speciation and removal efficiency are strongly dependent on the coal type.<sup>17</sup> Figure 4 compares the variation of  $\text{Hg}(0)/\text{Hg}(\text{VT})$  of coals and ashes with different chlorine and sulfur contents. It includes the following: a plot of  $\text{Hg}(0)/\text{Hg}(\text{VT})$  versus the different chlorine contents in the coal and ash (Figure 4a), a plot of  $\text{Hg}(0)/\text{Hg}(\text{VT})$  versus the different sulfur contents in the coal and ash (Figure 4b), and a plot of  $\text{Hg}(0)/\text{Hg}(\text{VT})$  versus the weight ratio of the



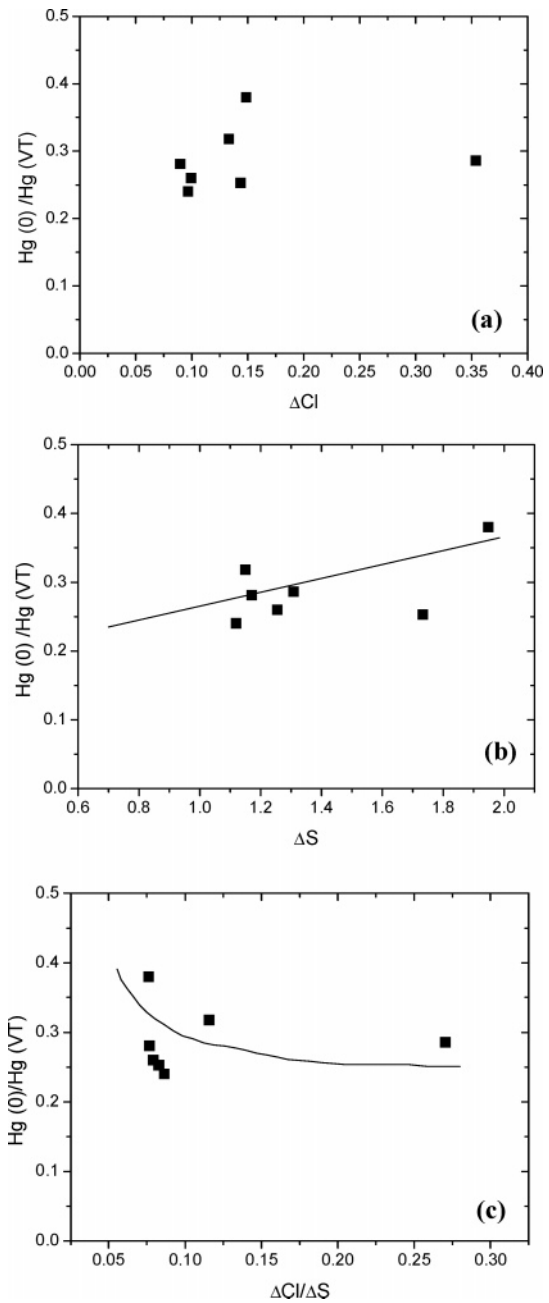
**Figure 3.** Relationship between gaseous mercury speciation at the ESP outlet location with (a) hydrogen chloride (HCl), (b) sulfur dioxide (SO<sub>2</sub>), and (c) the ratio of hydrogen chloride and sulfur dioxide (HCl/SO<sub>2</sub>) in the flue gas at test location 3.

chloride emitted in the gas phase to that of the sulfur in coal (Figure 4c).

The emitted amounts of chlorine and sulfur in the gas phase were calculated as follows:

$$\Delta\text{Cl} = \frac{\text{Cl}_{\text{in coal}} - \text{Cl}_{\text{in ash}} \times A_{\text{in coal}}}{1 - C_{\text{in ash}}} \quad (1)$$

$$\Delta\text{S} = \frac{\text{S}_{\text{in coal}} - \text{S}_{\text{in ash}} \times A_{\text{in coal}}}{1 - C_{\text{in ash}}} \quad (2)$$

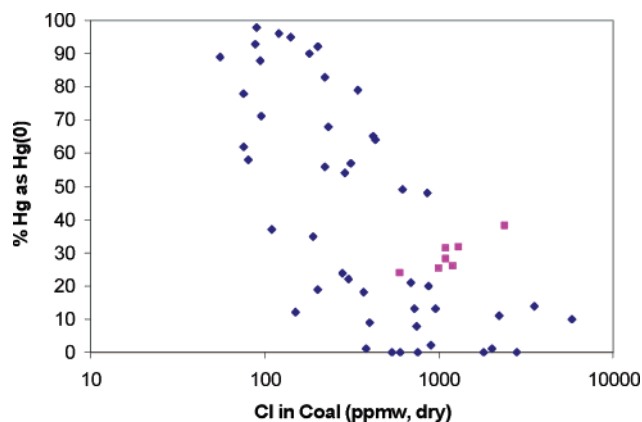


**Figure 4.** Relationship between average gaseous mercury speciation at the ESP outlet location with the difference between (a) chlorine content in coal and ash, (b) sulfur content in coal and ash, and (c) the ratio of the differences between the chlorine and sulfur contents (ΔCl/ΔS) in coal and ash.

where  $\text{Cl}_{\text{in coal}}$  is the chlorine content in the coal,  $\text{Cl}_{\text{in ash}}$  the chlorine content in the ash,  $A_{\text{in coal}}$  the ash content from the coal, and  $C_{\text{in ash}}$  the carbon content in the ash.  $\text{S}_{\text{in coal}}$  is the sulfur content in the coal and  $\text{S}_{\text{in ash}}$  is the sulfur content in the ash. All of these values are given in weight percent.  $\Delta\text{Cl}$  is the difference of the chlorine content in the coal and the ash produced, and  $\Delta\text{S}$  is the difference between the sulfur content in the coal and the ash produced; both of these differences are nondimensional parameters.

It is generally accepted that chlorine has a positive affect on mercury oxidation, based on the EPRI-ICR database.<sup>17</sup> However, as shown in Figure 4a, there is no apparent relationship between the mercury speciation and  $\Delta\text{Cl}$  for coals with >1000 ppm Cl. This





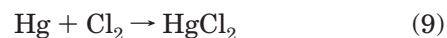
**Figure 5.** Effect of chlorine content in coal on gaseous mercury speciation at the ESP outlet (EPA-ICR data given in blue, WKU data given in red).

relationship also seems to be true when the mercury speciation is compared to the HCl concentration in the flue gas, as shown in Figure 3a. However, there is a significant decrease in elemental mercury with increasing coal chlorine content, as illustrated in Figure 5. This figure shows data from the EPA-ICR database<sup>31</sup> and results from this work. Figure 5 also shows that the effect of coal chlorine on the oxidation of elemental mercury in the flue gas may reach a maximum at coal chlorine concentrations of  $\sim 1000$  ppm, because the percentage of elemental mercury remaining in the flue gas approaches zero in some cases. In addition, most kinetic models<sup>7,32</sup> and the ICR database exclude the possibility that the reaction of chlorine species with mercury is kinetically limited. Therefore, it could be logically inferred that factors other than HCl concentration may affect mercury transformation chemistry, such as flue gas residence time in the downstream duct in different test units and other gas compositions in the flue gas. In this paper, one such factor that was emphasized is the sulfur species.

Chlorine in coal occurs in two main forms: (1)  $\text{Cl}^-$  ions that occur as alkali and alkaline-metal halides dissolved in pore water; and (2) chlorine enriched in organic matter, most likely as  $\text{Cl}^-$  ions absorbed on the inner surfaces of micropores in macerals.<sup>33</sup> During combustion, chlorine in coal is initially emitted primarily as atomic chlorine, which then forms HCl or molecular  $\text{Cl}_2$ , as shown in reactions 3–6.<sup>34</sup>

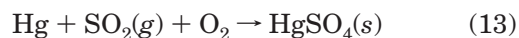
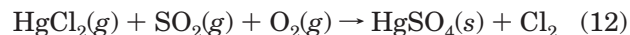


At the same time, elemental mercury from the coal reacts with chlorine species to form oxidized mercury, as shown in reactions 7–10.



Thermodynamic analysis and calculations predict that, in a typical combustion environment, almost all elemental mercury should be converted to oxidized mercury at temperatures of  $<450^\circ\text{C}$ , which is typical of temperatures downstream of the duct. However, based on available ICR data and our previous studies,<sup>17,19</sup> elemental mercury still exists at the stack with a temperature of  $<120^\circ\text{C}$ . It is believed that the reaction illustrated by reaction 7 is the initial step of the mercury oxidation process, because of its fast rate.<sup>17</sup> The slower reactions, represented by reactions 8, 9, and 10, dominate the overall oxidation process.<sup>17,35</sup> This provides some evidence that the mercury oxidation process in the combustion process is kinetically limited, although the oxidation process is thermodynamically favored. It also seems that the pool of Cl atoms is the key factor that controls the oxidation process of elemental mercury in high-temperature combustion processes. The slow reaction of reaction 8 dominates the oxidation mechanism in the downstream flue gas duct as the flue gas cools in the post-combustion area, where molecular chlorine may be formed by reactions illustrated by reactions 4 or 6. Thus, the short life span of Cl atoms in the flue gas upstream and the short residence time of the flue gas downstream in the combustion process limit the completion of the oxidation process of elemental mercury.

Although chlorine species dominate the oxidation of elemental mercury, other flue gas components, such as  $\text{SO}_2$ , NO, and  $\text{H}_2\text{O}$ , may also affect homogeneous mercury oxidation. As for  $\text{SO}_x$  emissions, it increases from 600 ppm for coal 4 and coal 5 to 1300 ppm for coal 7, as listed in Table 4. A trend seems to exist when one compares mercury speciation with  $\text{SO}_2$  concentrations in the flue gas or sulfur content in the coals, as shown in Figures 3b and 4b. With an increase in the sulfur content, the gaseous elemental mercury percentage increased, indicating that the conversion of elemental mercury to oxidized mercury was inhibited. Possible reactions that indicate the participation of  $\text{SO}_2$  and  $\text{O}_2$  in the conversion of elemental mercury to oxidized mercury are illustrated by reactions 11, 12, and 13.



$\text{SO}_2$  could likely reduce  $\text{Cl}_2$  in the flue gas, as suggested

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by reaction 11. Lowering the  $\text{Cl}_2$  content in the flue gas results in the reduced oxidation of mercury.<sup>36</sup> Elemental mercury and oxidized mercury could also react with  $\text{SO}_2$  and  $\text{O}_2$  to form the less-volatile  $\text{HgSO}_4$  solid via two paths, as illustrated by reactions 12 and 13. However, the path favored in the combustion process has not been determined. Presently, the speciation method for mercury in ash is still being studied.<sup>37</sup>

As a way of expressing the effects of chlorine and sulfur species on mercury speciation transformation, a new parameter—the  $\text{HCl}/\text{SO}_2$  ratio, as determined by the molar ratio in the flue gas and by the weight in the solid phase—was chosen to replace  $\text{HCl}$  in Figure 3a, and the results are plotted in Figure 3c. Similarly,  $\Delta\text{Cl}/\Delta\text{S}$  was plotted in Figure 4c. In this study, with an increase in the  $\text{HCl}/\text{SO}_2$  ratio, the portion of elemental mercury decreased significantly if the ratio was  $<0.15$  and was fairly constant for ratios of  $>0.15$ . The data suggest the oxidation of elemental mercury may have reached a maximum at this point.

Gaseous mercury speciation may also be affected by fly ash materials, as the result of elemental mercury interaction with active catalytic sites in ash, such as  $\text{CuO}$  and  $\text{Fe}_2\text{O}_3$ .<sup>38,39</sup> On the other hand, the formation of  $\text{Cl}_2$ , as illustrated in reaction 6, may also be enhanced in the presence of  $\text{CuO}$  and  $\text{Fe}_2\text{O}_3$ . The molecular chlorine ( $\text{Cl}_2$ ) readily reacts with mercury, as shown in reaction 9.  $\text{TiO}_2$  and  $\text{V}_2\text{O}_5$  have also been shown to be catalysts for mercury oxidation. Trace quantities of these oxides are in all seven fly ashes; thus, no conclusion can be made about the influence of  $\text{TiO}_2$  and  $\text{V}_2\text{O}_5$  on mercury oxidation in this study. Noting that the elemental mercury percentage was less than the mathematical fit trend line in Figure 3c for coal 2 and coal 5, it can be speculated that this may be due to the higher  $\text{Fe}_2\text{O}_3$  contents in the fly ashes of coal 2 and coal 5, as shown in Table 2. However, this conclusion must be validated by further investigation.

**Data Collected by the PS Analytical Semi-continuous Emissions Monitoring System.** The EPA OHM procedure was developed to measure stack mercury emissions and speciation in coal-fired utility boilers accurately. It cannot provide real-time continuous data and is a time-intensive procedure. The PS Analytical SCEM method can give almost-real-time, consecutive, and long-term results.

Mercury emission and speciation from the combustion of the test coals were continuously monitored using the PSA SCEM system, with the OHM procedure as a reference. The SCEM system was operated successfully for two short-term runs (5 days) for coal 2 and coal 4, and three long-term runs (10 days) for coal 3, coal 6,

and coal 7. The short-term runs and long-term runs were actually dependent on coal supplies at the power plant. Examples of the mercury test results for coal 3 (long-term testing) and coal 4 (short-term testing) at the ESP outlet location are shown in Figure 6. Analysis of the data shows that mercury emission varied with the boiler load. As the boiler load decreased, the mercury emissions for both total and elemental mercury also decreased, because of a longer residence time in the duct at the lower power output. With a longer residence time, the total gaseous mercury would have a better chance of being absorbed on the fly ash and the elemental mercury would have a greater chance of being oxidized. Also note that, as the boiler load decreased, the air/coal ratio was increased and, thus, the mercury concentration in the flue gas was diluted by excess air. Therefore, to monitor mercury emissions in the utility boiler, an 80%–100% boiler load should be maintained, so that misleading data are not collected.

The mercury emissions varied for all test coals. While the boiler load was maintained in the range of 80%–100%, the ratio of maximum to minimum was  $\sim 2$  for total gaseous mercury and 3–4 for gaseous elemental mercury, with a maximum/minimum ratio of  $\sim 5$  for the overall testing period for each run. However, with respect to probability analysis, the SCEM data seemed reasonable, because a large number of points were located in its average range with a narrow bell-type distribution. The gaseous elemental mercury had a smaller standard deviation than the total gaseous mercury.

**Comparison of the Ontario Hydro Method and Semi-continuous Emissions Monitoring Test Results.** One important function of this study was to compare the OHM and SCEM results. Table 5 gives a summary of the test results at the ESP outlet for both methods. As previously mentioned, the number of test runs per coal was dependent on the type of coal, the planned experiment for each coal, the availability of the coal with proper boiler load, and other factors. Relative error, as defined by eq 14, is a way to compare experimental results between the two sampling methods.

$$\text{relative error} = 100 \times \frac{\text{OHM data} - \text{SCEM data}}{\text{OHM data}} \quad (14)$$

Using OHM data as the denominator does not imply that the OHM data are more accurate than the SCEM data, although the denominator in the relative error equation is generally the “accepted” value. An analysis of the data revealed that agreement between the two methods seemed to be dependent on the test location.

Table 6 shows the calculated relative errors between the OHM and SCEM methods at the ESP outlet and ESP inlet for the seven coals. The values show reasonable agreement for the measurement of total gaseous mercury ( $\text{Hg}(\text{VT})$ ) at the ESP outlet, with the relative error ranging from a low of  $-33.3\%$  for coal 5 to a high of  $26.9\%$  for coal 6. At the ESP inlet, a similar comparison shows that the relative error for total gaseous mercury between the two methods ranged from a low of  $-346\%$  for coal 4 to a high of  $23.8\%$  for coal 6. The flue gas at the ESP inlet was heavily laden with fly ash, which affected the monitoring of gaseous mercury, as sampled by the two methods. Other comparisons can be made

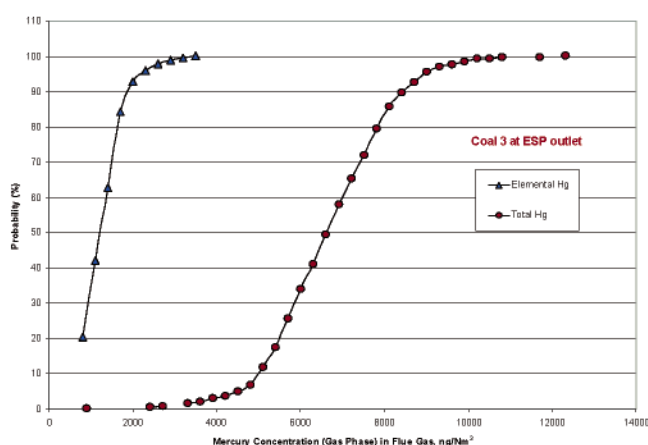
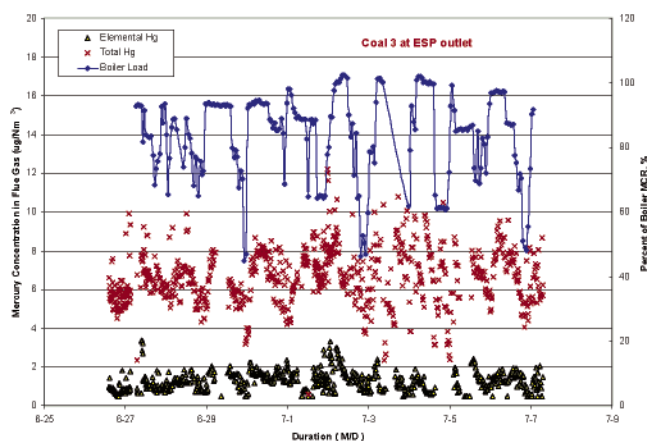
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## Coal #3



## Coal #4

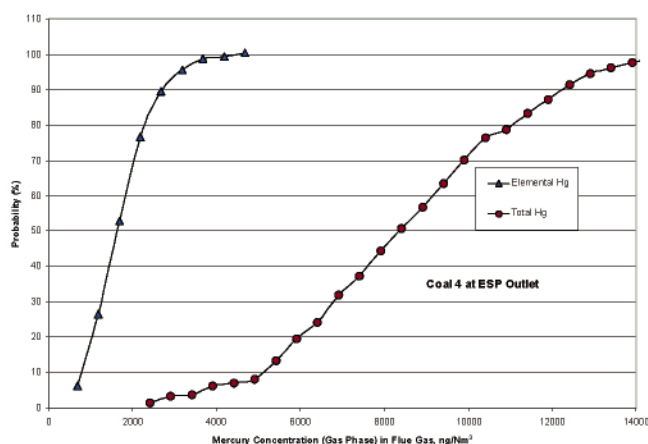
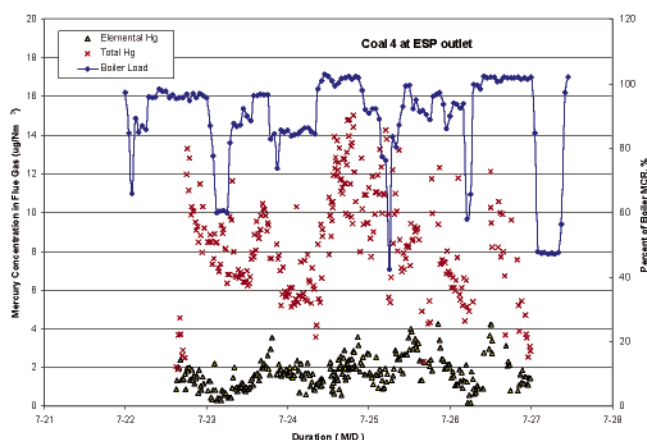


Figure 6. Test results for two coals monitored by the PSA SCEM at the ESP outlet location.

for elemental mercury and oxidized mercury, but a more meaningful comparison can be made by considering the entire set of data in Table 6.

In Table 6, the values for coal 4 at the ESP inlet are an order of magnitude different from the other data and can be considered as outliers. Similarly, the Hg(0) data for coal 3 can also be considered as outliers. Reasons for the differences in data will be discussed later. The modified averages for the remaining data in Table 6 do indicate significant trends. The small numbers for the averages indicate that the errors between the OHM and SCEM measurements for Hg(VT) and Hg(2+) are probably random, with small biases. The averages for Hg(0) are larger, indicating larger biases; however, it must be considered that the absolute values for Hg(0) are so small that the relative errors are magnified. A case can be made that the biases (average errors) of 3.0, 7.1, and 36.1 for Hg(VT), Hg(2+), and Hg(0), respectively, at the ESP outlet are more positive than the corresponding values of -7.1, 2.5, and -15.3 for the same species at the ESP inlet.

**Ontario Hydro Method versus Semi-continuous Emissions Monitoring, and the Role of Measurement Location.** At the ESP outlet, the difference between the OHM and SCEM results could be due to several factors that are present in the two sampling activities. The SCEM uses a long heated transfer, line

over which it is possible that some cool spots may exist. The cool spots may allow moisture and SO<sub>3</sub> to condense and trap mercury. Long-term runs could allow soot buildup from the flue gas passing through the filtration system of the SCEM, which could also capture mercury. Both of these factors will cause a negative bias in the mercury concentration measured in the flue gas. Also, the PSA SCEM uses a sodium hydroxide (NaOH) solution in its mercury speciation module, which will react with CO<sub>2</sub>, which constitutes ~15% of the flue gas. Consequently, the volume of the flue gas is decreased, and the reported mercury concentration in the flue gas, as measured by the SCEM analyzer, is higher than the actual mercury concentration in the flue gas. This factor will cause a positive bias in the SCEM measurement. In the majority of cases, as shown in Table 5, the OHM gives higher mercury concentrations in the flue gas than SCEM. The modified averages in Table 6 indicate the same trend for the ESP outlet location, because they are all positive. However, the modified averages for the ESP inlet show negative biases for Hg(VT) and Hg(0), indicating the OHM gives lower values than SCEM. These results are a combination of the factors mentioned, plus other factors that are unknown at this time.

For most coals, the OHM measured a lower level of total gaseous mercury and elemental mercury than did SCEM at the ESP inlet, but higher levels at the ESP

**Table 5. Test Results for Mercury Emission and Speciation Using the OHM and SCEM at the ESP Outlet Location**

	SCEM					OHM					
	test 1	test 2	test 3	test 4	average	test 1	test 2	test 3	test 4	test 5	average
Coal 1; Location: ESP Outlet											
Hg(VT) (ng/Nm <sup>3</sup> ) <sup>a</sup>	11049	12699	14112	9517	11844	10455	11808	12595	13309	10074	11648
Hg(2+) (ng/Nm <sup>3</sup> ) <sup>a</sup>	8208	10205	10979	8143	9384	7331	8856	9262	10258	7417	8625
Hg(0) (ng/Nm <sup>3</sup> ) <sup>a</sup>	2841	2493	3133	1374	2460	3124	2952	3333	3050	2657	3023
Hg(0)/Hg(VT) (%)	26	20	22	14	20	30	25	27	23	26	26
Coal 2; Location: ESP Outlet											
Hg(VT) (ng/Nm <sup>3</sup> ) <sup>a</sup>	7002	7131	9814	8496	8111	9133	9931				9532
Hg(2+) (ng/Nm <sup>3</sup> ) <sup>a</sup>	6215	6138	9189	7501	7261	6784	7459				7121
Hg(0) (ng/Nm <sup>3</sup> ) <sup>a</sup>	787	993	625	995	850	2349	2472				2411
Hg(0)/Hg(VT) (%)	11	14	6	12	10	26	25				25
Coal 3; Location: ESP Outlet											
Hg(VT) (ng/Nm <sup>3</sup> ) <sup>a</sup>	9418	9418		6262	8366	10284	8214	9763	7932		9048
Hg(2+) (ng/Nm <sup>3</sup> ) <sup>a</sup>	7427	7427		5076	6643	7813	5923	6855	5419		6503
Hg(0) (ng/Nm <sup>3</sup> ) <sup>a</sup>	1992	1992		1185	1723	2471	2290	2907	2513		2545
Hg(0)/Hg(VT) (%)	21	21		19	20	24	28	30	32		28
Coal 4; Location: ESP Outlet											
Hg(VT) (ng/Nm <sup>3</sup> ) <sup>a</sup>	9897	8398	10910		9735	11614	14953				13283
Hg(2+) (ng/Nm <sup>3</sup> ) <sup>a</sup>	8357	6903	8916		8059	7751	10384				9067
Hg(0) (ng/Nm <sup>3</sup> ) <sup>a</sup>	1540	1494	1993		1676	3863	4569				4216
Hg(0)/Hg(VT) (%)	16	18	18		17	33	31				32
Coal 5; Location: ESP Outlet											
Hg(VT) (ng/Nm <sup>3</sup> ) <sup>a</sup>	5715	5000			5357	4460	3580				4020
Hg(2+) (ng/Nm <sup>3</sup> ) <sup>a</sup>	4085	4441			4263	3180	2940				3060
Hg(0) (ng/Nm <sup>3</sup> ) <sup>a</sup>	1629	559			1094	1280	640				960
Hg(0)/Hg(VT) (%)	29	11			20	29	18				23
Coal 6; Location: ESP Outlet											
Hg(VT) (ng/Nm <sup>3</sup> ) <sup>a</sup>	8339	8636	9844		8940	14320	11790	10590			12233
Hg(2+) (ng/Nm <sup>3</sup> ) <sup>a</sup>	6501	5429	7935		6622	10220	7370	7550			8380
Hg(0) (ng/Nm <sup>3</sup> ) <sup>a</sup>	1838	3207	1909		2318	4090	4420	3050			3853
Hg(0)/Hg(VT) (%)	22	37	19		26	29	37	29			31
Coal 7; Location: ESP Outlet											
Hg(VT) (ng/Nm <sup>3</sup> ) <sup>a</sup>	27448	29773			28611	26110	23610	23530	22050		23825
Hg(2+) (ng/Nm <sup>3</sup> ) <sup>a</sup>	23541	24862			24202	16190	14640	14180	14140		14788
Hg(0) (ng/Nm <sup>3</sup> ) <sup>a</sup>	3907	4911			4409	9920	8970	9340	7910		9035
Hg(0)/Hg(VT) (%)	14	16			15	38	38	40	36		38

<sup>a</sup> Includes 3% O<sub>2</sub> correction.**Table 6. Relative Errors between OHM and SCEM Systems at ESP Outlet and Inlet**

coal	Hg(VT) Relative Errors		Hg(2+) Relative Errors		Hg(0) Relative Errors	
	ESP outlet	ESP inlet	ESP outlet	ESP inlet	ESP outlet	ESP inlet
1	-1.7	5.8	-8.8	14.7	18.6	-72.5
2	14.9	-13.4	-2.0	-13.8	64.7	-9.1
3	7.5	-55.5	-2.2	-9.1	32.3	-580.1
4	26.7	-346.4	11.1	-256.8	60.3	-994.8
5	-33.3	-12.3	-39.3	-9.0	-14.0	-27.2
6	26.9	23.8	21.0	19.0	39.8	43.4
7	-20.1	9.0	70.2	13.4	51.2	-11.3
average	3.0	-55.6	7.1	-34.5	36.1	-235.9
average <sup>a</sup>	3.0	-7.1	7.1	2.5	36.1	-15.3

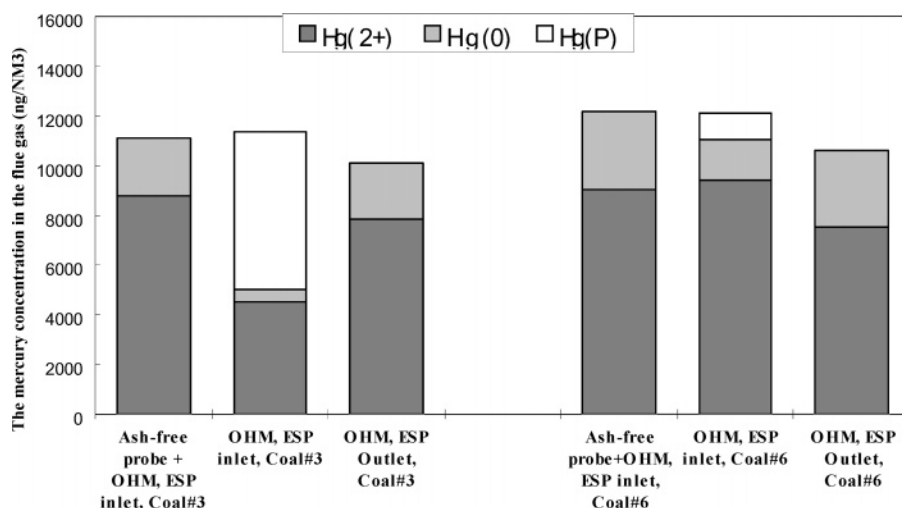
<sup>a</sup> ESP inlet values for coal 4 were not included, nor was the Hg(0) value for coal 3 at the ESP inlet.

outlet. A major difference between the two test locations is the level of fly ash in the flue gas, with the level at the ESP inlet being much greater than that at the ESP outlet. The average flue gas fly ash concentration was 7.40 g/Nm<sup>3</sup> at the ESP inlet but was below the detection limit of the OHM at the ESP outlet. Fly ash may capture mercury at lower temperatures and also has a catalytic effect on the conversion of elemental mercury to oxidized mercury. How the two methods remove fly ash is an important difference between them. The OHM uses a static filter, where fly ash accumulates throughout the test period. In contrast, SCEM uses an ash-free probe that eliminates a majority of the ash effects. Therefore, the possibility of fly ash buildup is much greater in the OHM sampling process, which allows more opportunity

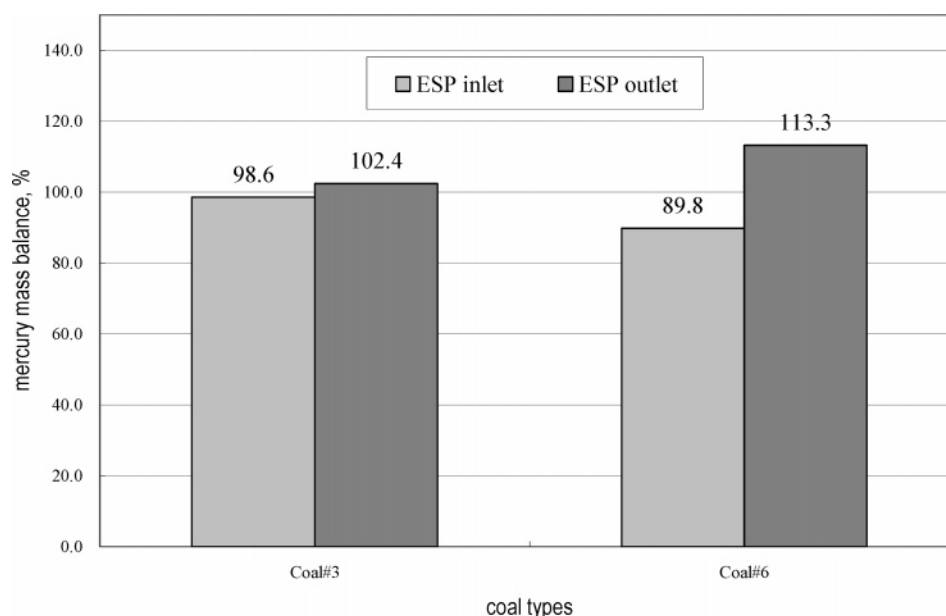
for gaseous mercury to become particle-bound mercury and elemental mercury to become oxidized mercury.

It is assumed that, when the probe of the OHM is replaced with an ash-free flue gas sampling probe in high-ash-load situations, the ash-induced bias could be greatly diminished, because gaseous mercury would not be absorbed by ash carbon, as it is using the OHM standard probe. To get precise information on mercury speciation of particle-bound mercury, elemental vapor mercury, and oxidized mercury, a combined method of measurement was conducted. In the combined method, an OHM standard probe was used to collect total mercury, including particle-bound and vapor-phase mercury (Hg(T)). The ash-free probe with the OHM impinger train was used to determine total vapor-phase





**Figure 7.** Comparison of mercury concentrations collected using the Ontario Hydro Method (OHM) with the regular filter and an ash-free probe for coal 3 and coal 6.



**Figure 8.** Mercury mass balance at locations of the ESP inlet and outlet for coal 3 and coal 6.

mercury ( $\text{Hg(VT)}$ ) and the concentrations of gaseous mercury species. The difference between the  $\text{Hg(T)}$  from the OHM and the  $\text{Hg(VT)}$  from the ash-free method is the particle-bound mercury. With the results of the combined OHM tests, the absorption ratio of different gaseous mercury species could be calculated. The test results for coal 3 and coal 6 are shown in Figure 7. However, this newly developed method for the accurate estimation of mercury speciation in high-ash-load situations should be further verified.

After careful organization of sampling results from all the mercury streams, good mercury mass balances (within  $\pm 20\%$ ) were obtained. For example, the mass balances for two test coals (coal 3 and coal 6) at two test locations are shown in Figure 8. The mercury mass balance is based on the total mercury input from the coal, the total mercury output in the flue gas, including the sum of the mercury in the gas and particle-bound phases at the designated sampling locations and mercury in ash samples collected from the flue gas duct in front of the sampling locations. The mercury mass balance values are presented as total mercury output

divided by total mercury input. At the ESP inlet location, the ash collected prior to the sampling location was the mechanical hopper ash, and at the ESP outlet location, the ash collected prior to the sampling location was the mechanical hopper ash and ESP ash.

Note that the elemental mercury seems to be easily associated with the fly ash using the modified OHM, as shown in Figure 7. It is generally accepted that oxidized mercury is more likely to be bound on the fly ash at lower temperatures. For example, unburned carbon in the fly ash shows no tendency to absorb elemental mercury but readily absorbs oxidized mercury. One possible mechanism for this to occur is that the fly ash can catalyze the oxidation of elemental mercury to oxidized mercury, allowing it to be more easily absorbed by the fly ash as the flue gas passes through the fly ash carbon on the OHM filter.

#### 4. Conclusions

Seven coals with chlorine contents ranging from 0.09 to 0.36 wt % and sulfur contents ranging from 1.2% to 2.0% were burned in a 100-MW full-scale utility boiler

with low- $\text{NO}_x$  burners and cold-side electrostatic precipitators (ESPs) to investigate mercury emission, transformation, and speciation. The gaseous mercury speciation was affected by the sulfur and chlorine concentrations in the flue gas, as well by as the ash properties. Chlorine in the coals was determined to promote the mercury oxidation process. However, high sulfur concentrations in the flue gas from the utility boiler inhibited the chlorine-promoted mercury oxidation process.

(1) The coal chlorine content does have an impact on the mercury oxidation processes, which are mitigated by high concentrations of  $\text{SO}_2$ . It is speculated that  $\text{SO}_2$  limits  $\text{Cl}_2$  formation, which is one of the more likely species to convert elemental mercury to oxidized mercury in the flue gas. It was determined that 20%–35% of the total gaseous mercury was elemental mercury in this study.

(2) In addition to the impact of the flue gas components, gaseous mercury speciation could also be affected by ash properties.  $\text{Fe}_2\text{O}_3$  seems to promote the oxidation of elemental mercury in the flue gas.

(3) A sampling bias was observed in the Ontario Hydro Method (OHM) sampling that was performed at the ESP inlet, because of the accumulation of ash with a high carbon content on the OHM filter. An ash-free sampling probe should be used with the OHM impinger train to obtain accurate mercury information whenever ash concentrations are high.

(4) Semi-continuous emissions monitoring (SCEM) was operated continuously for the long-term monitoring of mercury emission and speciation. Statistical analysis of the SCEM data shows that the majority of the data had a small variation from the average. The mercury value in the flue gas varied with the boiler load. When the boiler load was down, the mercury concentration also decreased. Comparison of test results from the

OHM and SCEM procedures at the ESP outlet showed that good agreement between the methods could be reached. However, at the ESP inlet, a lower concentration of gaseous mercury was consistently measured by the OHM. A possible reason for this is that the ash deposits on the OHM filter at the ESP inlet may change the total mercury speciation.

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