



Evaluation of mercury speciation and removal through air pollution control devices of a 190 MW boiler

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Abstract

Air pollution control devices (APCDs) are installed at coal-fired power plants for air pollutant regulation. Selective catalytic reduction (SCR) and wet flue gas desulfurization (FGD) systems have the co-benefits of air pollutant and mercury removal. Configuration and operational conditions of APCDs and mercury speciation affect mercury removal efficiently at coal-fired utilities. The Ontario Hydro Method (OHM) recommended by the U.S. Environmental Protection Agency (EPA) was used to determine mercury speciation simultaneously at five sampling locations through SCR-ESP-FGD at a 190 MW unit. Chlorine in coal had been suggested as a factor affecting the mercury speciation in flue gas; and low-chlorine coal was purported to produce less oxidized mercury (Hg^{2+}) and more elemental mercury (Hg^0) at the SCR inlet compared to higher chlorine coal. SCR could oxidize elemental mercury into oxidized mercury when SCR was in service, and oxidation efficiency reached 71.0%. Therefore, oxidized mercury removal efficiency was enhanced through a wet FGD system. In the non-ozone season, about 89.5%–96.8% of oxidized mercury was controlled, but only 54.9%–68.8% of the total mercury was captured through wet FGD. Oxidized mercury removal efficiency was 95.9%–98.0%, and there was a big difference in the total mercury removal efficiencies from 78.0% to 90.2% in the ozone season. Mercury mass balance was evaluated to validate reliability of OHM testing data, and the ratio of mercury input in the coal to mercury output at the stack was from 0.84 to 1.08.

Key words: mercury speciation; mercury removal; air pollution control device; field testing

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Introduction

Mercury emissions are regarded as one of the most problematic environmental issues in the world because of their propensity towards bio-accumulation within an aquatic food chain. After bio-accumulation, mercury may result in neuron damage to humans (Cao et al., 2005). It is estimated that 80% of the total anthropogenic mercury emissions from 1994 to 1995 was from combustion, of which 33% was associated with coal-fired utility boilers. The U.S. EPA officially announced the Clean Air Mercury Rule (CAMR) in March 2005 for mercury sequestration that applies to coal-fired power plants. CAMR establishes a cap-and-trade program for national emissions of Hg, with national caps set in two phases: 38 tons per year starting in 2010 and 15 tons per year starting in 2018 (Zhou et al., 2007). Recently, a federal court overturned the EPA's rule controlling mercury emissions from coal-fired power plants. Based on the explicit act of U.S. Congress, it is likely that EPA will be required a more stringent control rule on mercury emissions. Mercury

species in coal-fired flue gas include elemental, oxidized and particulate-bound mercury. Mercury is removed across power plants' conventional air pollution control devices (APCDs) such as selective catalytic reduction (SCR), electrostatic precipitator (ESP), fabric filters (FF) and flue gas desulfurization (FGD) systems. SCR used for control of NO_x emissions may further enhance mercury capture by oxidizing elemental mercury across the SCR catalyst (Zhuang et al., 2007; Pavlish et al., 2003). The SCR is in service during the ozone season (May 1st–Sept 30th) in the U.S., while the SCR is bypassed in other times. Extensive mercury tests showed that APCDs installed for removing NO_x, SO_x, and particulate matter (PM) can achieve the co-benefits of mercury capture (Romero et al., 2006; Diaz-Somoano et al., 2003).

To better understand mercury capture through conventional APCD systems, field testing was performed at a 190 MW cyclone unit equipped with an SCR-ESP-WFGD combination at a coal-fired power plant, and mercury speciation and mercury removal through the typical SCR-ESP-WFGD were evaluated. The Ontario Hydro Method (OHM) was used to determine mercury emissions and

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speciation at five sampling locations, and OHM quality assurance/quality control (QA/QC) was followed during the field testing.

1 Materials and methods

1.1 Unit and coal sample

A 190 MW cyclone boiler with common air pollution control devices (SCR, cold-ESP and wet FGD with limestone natural oxidation system) was chosen to test mercury speciation and mercury removal status.

Coal samples were collected during two sampling periods (ozone and non-ozone season) respectively. Fly ash, bottom ash and wet FGD slurry samples were also collected to obtain the mercury balance across the APCDs. Table 1 lists the proximate and ultimate analysis as well as Hg/F/Cl concentration of both coal samples. The analysis results of two coal samples were similar except for different chloride concentrations in the coal samples. Chloride content was 312.10 mg/kg in the coal sample collected in the non-ozone season, but was 1248.33 mg/kg in the coal sample collected in the ozone season.

1.2 Sampling method and locations

The OHM that has been approved by ASTM (Method D6784) is the only EPA reference method for measuring mercury speciation in flue gas, and OHM is a wet chemistry method used to collect vapor mercury speciation (elemental mercury and oxidized mercury). Gas samples were withdrawn from the flue gas stream iso-kinetically. Oxidized mercury was collected in the first three impingers containing a chilled aqueous potassium chloride solution, because oxidized mercury was water soluble. Elemental mercury was collected in subsequent impingers (one impinger containing a chilled aqueous acidic solution of hydrogen peroxide and three impingers containing chilled aqueous acidic solutions of potassium permanganate)

because elemental mercury was oxidized into oxidized mercury and Hg^{2+} was trapped in the solution. The liquid solutions were recovered and digested by an automated mercury preparation system; then solutions were analyzed by cold vapor atomic absorption spectroscopy (CVAAS) (Leeman Lab Hydra, Teledyne Leeman Labs, NH). In order to evaluate mercury speciation through a series of APCD systems on the same basis, all the OHM data at five sampling locations were corrected to a 3% oxygen basis in the flue gas. Mercury tests were performed during the normal operation of the 190 MW boiler, and the boiler was kept running at almost full and stable load during OHM sampling time. Sampling locations of vapor mercury measurement were the SCR inlet and outlet, ESP inlet, FGD inlet and the stack. The OHM sampling of EPA QA/QC procedures was followed throughout all these tests. OHM sampling at five locations was conducted simultaneously during the non-ozone and ozone season. Testing locations are shown in Fig. 1.

2 Results and discussion

2.1 Transformation of mercury speciation through the SCR system

The mercury tests were performed at non-ozone and ozone seasons respectively. The comparisons of mercury speciation at the SCR inlet are shown in Fig. 2. The results indicate that the elemental mercury was the predominant mercury speciation (Fig. 2a) from 74.0% to 98.0% when SCR was bypassed. However, the fraction of elemental mercury in the total mercury ranged from 30.0% to 70.0% when SCR was in service (Fig. 2b). In general, oxidized mercury percentage in flue gas during the ozone season was larger than it during the non-ozone season. The sharp change of mercury speciation in the flue gas was related to chloride content in coal because there was a big difference in chloride concentrations from the two coal samples.

Table 1 Coal samples analysis results

Coal sample collecting season	Proximate analysis (%)			Heat value (kJ/kg)	Ultimate analysis (%)					Hg (mg/kg)	F (mg/kg)	Cl (mg/kg)
	M_{ad}	A_{ad}	V_{ad}		C_{ad}	H_{ad}	N_{ad}	S_{ad}	O_{ad}			
Non-ozone	2.32	15.86	36.93	27714.38	68.15	4.64	1.22	3.46	6.68	0.09	119.60	312.10
Ozone	4.75	14.97	34.99	28857.68	69.45	4.72	1.15	3.04	6.67	0.11	105.67	1248.33

ad: air dry basis. M: moisture; A: ash content; V: volatile matter.

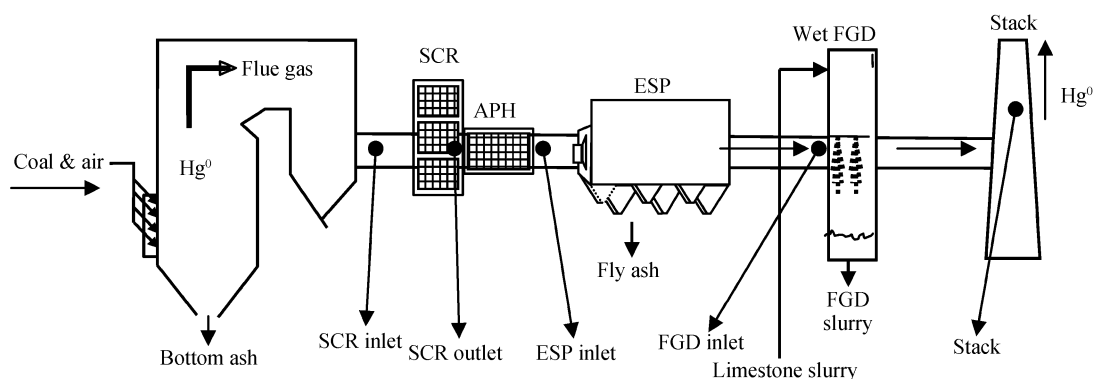


Fig. 1 Schematic description of unit and sampling locations.

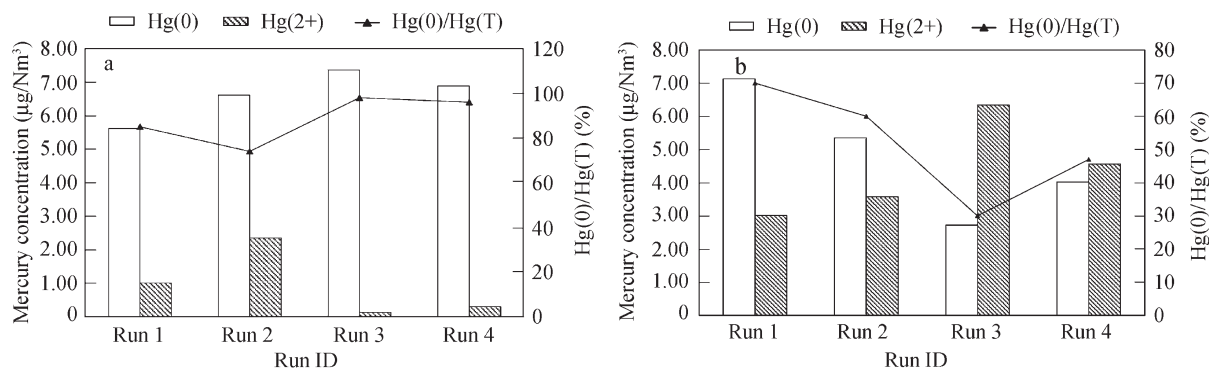


Fig. 2 Mercury speciation at SCR inlet in non-ozone season (a) and in ozone season (b).

Elemental mercury was converted into HgCl_2 by chloride (Cl , Cl_2 and HCl) in the boiler. This indicates that the concentration of chloride was the critical condition necessary to convert elemental mercury into oxidized mercury.

The mercury speciation at the SCR inlet and outlet during the ozone season is shown in Figs. 2b and 3. There was a significant difference in mercury speciation in the flue gas through SCR because a fraction of elemental mercury was oxidized catalytically by the SCR catalyst. The SCR catalyst consisted of metal oxides such as V_2O_5 and TiO_2 etc. (Yang and Pan, 2007). The mercury oxidation reaction occurred between vapor elemental mercury and acid gases such as HCl , HF and other hydrogen halides in flue gas. Mercury oxidation was dramatically enhanced, and about 80.0% of the total vapor mercury was presented in an oxidized mercury state (Fig. 3). Oxidation efficiencies of elemental mercury across SCR are shown in Fig. 3. Oxidation efficiency (η) was used to evaluate oxidation ability of elemental mercury across SCR, and it can be formulated as Eq. (1):

$$\eta = (\text{Hg}_{\text{SCR,outlet}}^{2+} - \text{Hg}_{\text{FGD,inlet}}^{2+}) / \text{Hg}_{\text{SCR,inlet}}^0 \quad (1)$$

The Hg^0 oxidation efficiency can reach 71.0% across the SCR system. Catalyst life, operational temperature and space velocity also affected oxidation efficiency of elemental mercury. Higher mercury oxidation efficiency in flue gas across the SCR can increase mercury removal efficiency through downstream ESP and wet FGD.

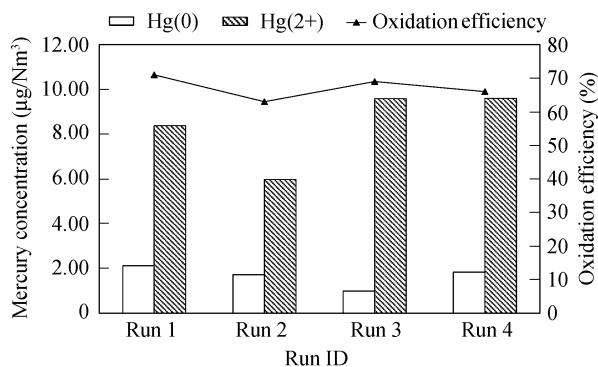


Fig. 3 Mercury speciation at SCR outlet and oxidation efficiency through SCR.

2.2 Mercury removal through cold-side ESP

Cold-side ESP was used to control particulate matter in coal-fired power plants. Mercury was adsorbed on the surface of fly ash; and the unburned carbon also affected mercury adsorption. Therefore, particulate-bound mercury was captured with fly ash. Unburned carbon, surface area and metal oxides in fly ash and operational temperature of ESP affected mercury removal efficiency across ESP. Mercury speciation at the cold-side ESP inlet and outlet in non-ozone and ozone seasons is shown in Fig. 4. Each set of bars in the figure represents gas-phase mercury concentration (elemental and oxidized mercury) at the ESP inlet and outlet for every run, and the values above each bar of the ESP outlet denote mercury removal efficiencies through cold-side ESP. Mercury removal efficiency through air pollution control devices was denoted as: $(\text{Hg}_{\text{inlet}}^T - \text{Hg}_{\text{outlet}}^T) / \text{Hg}_{\text{inlet}}^T$. Mercury removal efficiencies across the ESP were smaller in the non-ozone season than they were in the ozone season. Mercury removal efficiencies ranged from 2.61% to 5.83% in the non-ozone season, while mercury capture efficiencies ranged from 7.91% to 15.1% in the ozone season. Mercury speciation with/without SCR affected mercury removal through cold-side ESP. The reason was that different mercury speciation affected mercury absorption on fly ash. Unburned carbon in fly ash adsorbed elemental mercury, and a fraction of mercury was removed through cold-side ESP. On the other hand, ash composition, especially the basic ash compositions (CaO , Na_2O , K_2O , and Fe_2O_3) were key factors affecting mercury oxidation (Chen et al., 2007). Elemental mercury was oxidized into oxidized mercury in the non-ozone season, which limited mercury removal efficiency through ESP. However, mercury oxidation tested in the ozone season was not apparent. There were some test errors in mercury oxidation and mercury removal efficiency, which related to sampling probes. To get precise information on mercury speciation, the OHM regular probe and ash-free initial probe were used at the ESP inlet and outlet in the non-ozone and ozone season respectively. Fly ash deposited on the finger filter prevented the ash from pumping into the sampling instrument with sampling time when the OHM probe was used. This also allowed the flue gas to flow through fly ash accumulated on the finger filter. Fly ash captured mercury at lower temperatures and had a catalyst oxidation function of elemental mercury to

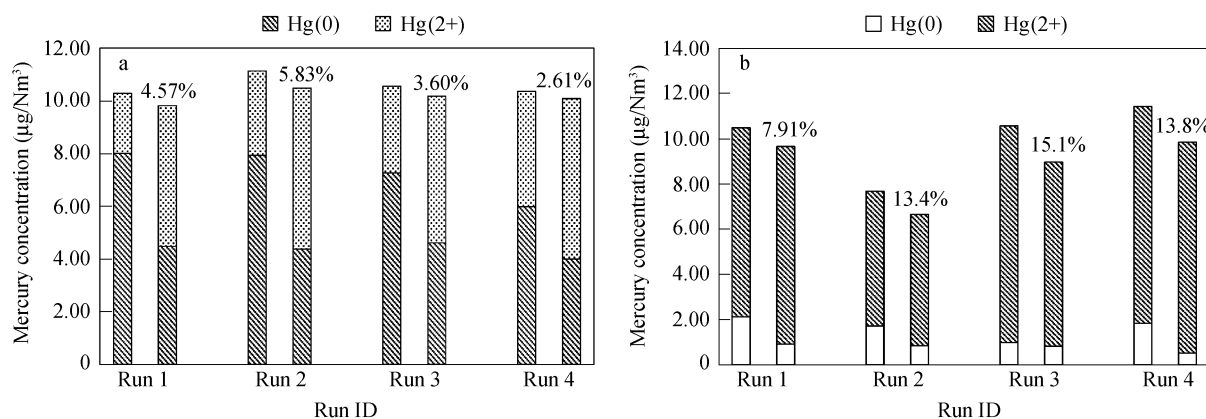


Fig. 4 Mercury speciation through cold ESP in non-ozone season (a) and ozone season (b). The percentage above second bar denotes the mercury removal efficiency across ESP.

oxidized mercury. An ash-free initial probe can prevent ash from depositing in the high temperature tube, greatly reducing the ash-induced bias.

2.3 Mercury emission through wet FGD

Oxidized mercury is water soluble, and wet FGD systems were effective at removing oxidized mercury, but not elemental mercury. Four mercury measurements were conducted at the FGD inlet and stack simultaneously in non-ozone and ozone seasons respectively, and mercury speciation was then analyzed. Mercury speciation and mercury capture efficiency through wet FGD with SCR was on and off are plotted in Fig. 5. Each set of bars in the figure represents gas-phase mercury concentration at the FGD inlet and stack for a given test. Each bar is further divided to show oxidized mercury and elemental mercury concentrations. Mercury removal efficiencies through wet FGD are displayed above the second bar. There was a high percentage of oxidized mercury at the FGD inlet in the flue gas with SCR online and oxidized mercury was significantly captured in the calcium-containing liquid slurry across the wet FGD because the oxidized mercury was soluble. Elemental mercury cannot be captured across wet FGD. Therefore, the Hg^0 concentrations should be similar at the FGD inlet and stack. However, the results showed that the elemental mercury at the stack, compared to the FGD inlet, was lower in some tests and higher in

others. Mercury capture efficiencies were different due to different mercury speciation in the flue gas upstream of wet FGD. Increases of oxidized mercury percentages in flue gas can enhance overall mercury removal across the wet FGD.

As shown in Fig. 5a, in the absence of the SCR system, elemental and oxidized mercury in the total mercury found in the flue gas at the FGD inlet and outlet and mercury removal efficiency are plotted. Elemental mercury cannot be absorbed in the slurry and emitted with flue gas. Although 89.5%–96.8% of oxidized mercury was controlled, only 54.9%–68.8% of the total mercury was captured through wet FGD because there was a lower fraction of oxidized mercury in the total mercury within the flue gas.

Figure 5b shows mercury speciation and removal efficiencies through wet FGD in the ozone season, when oxidized mercury removal efficiency was 95.9%–98.0%, but there was a significant difference in total mercury removal efficiencies from 78.0% to 90.2% because of elemental mercury fractions in the total mercury. Elemental mercury concentrations at the stack were higher than they were at the FGD inlet in Run 2 and Run 4. This may be because there were testing relative errors at the acceptable range of 20%; on the other hand, elemental mercury increased across wet FGD because a portion of oxidized mercury was reduced into elemental mercury in the FGD slurries, which was defined as mercury re-emission across

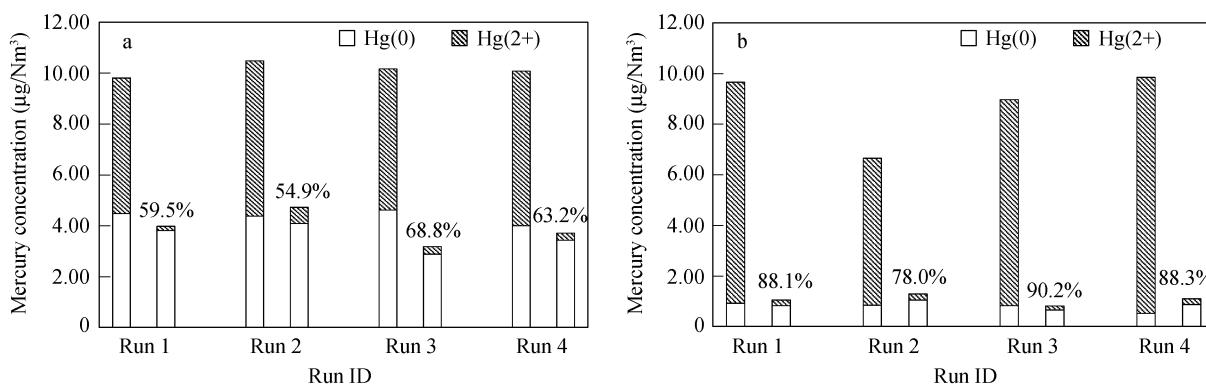


Fig. 5 Mercury speciation through wet FGD at non-ozone season (a) and ozone season (b). The percentage above second bar denotes the mercury removal efficiency across wet FGD.

Table 2 Mercury mass balance summary at stack

Test time	Hg in coal ($\mu\text{g}/\text{kg}$)	Hg outlet at stack				<i>R</i>
		Hg in flue gas ($\mu\text{g}/\text{kg}$ coal)	Hg in bottom ash ($\mu\text{g}/\text{kg}$ coal)	Hg in fly ash ($\mu\text{g}/\text{kg}$ coal)	Hg in FGD slurry ($\mu\text{g}/\text{kg}$ coal)	
Non-ozone season	90.0	36.42	0.07	0.86	59.08	1.07
	90.0	43.27	0.08	0.60	52.84	1.07
	90.0	29.10	0.08	1.27	65.04	1.06
	90.0	34.12	0.08	1.43	62.44	1.08
Ozone season	110.0	9.52	0.07	0.53	82.44	0.84
	110.0	11.71	0.08	0.84	90.27	0.93
	110.0	7.32	0.08	0.78	93.02	0.92
	110.0	9.97	0.09	0.65	90.67	0.92

wet FGD system. Mercury re-emission decreased overall mercury removal efficiency. Chemical additives such as NaHS and TMT15 were used to suppress mercury re-emission at coal-fired power plants with wet FGD systems (Renninger et al., 2004).

It was indicated that there was a significant effect of SCR on mercury removal efficiency across wet FGD. In order to increase mercury removal efficiency through wet FGD, high fractions of elemental mercury contained in the total mercury should be converted into oxidized mercury through devices upstream of wet FGD. Generally, if there is a higher fraction of oxidized mercury in the total mercury of flue gas, better mercury removal will be attained at some power plants with a SCR-ESP-WFGD system, which meet release requirements of EPA.

2.4 Mercury mass balance through coal-stack

In order to validate the reliability of OHM sampling data, mercury mass balance was conducted. The mercury mass balance evaluation through APCD was based on mercury analysis of the flue gas at the stack; both solid and liquid samples during the time of OHM sampling. The ratio of Hg outlet to Hg input at the stack was determined by Eq. (2):

$$R = M_{\text{Hg,outlet}}/M_{\text{Hg,inlet}} \quad (2)$$

where, $M_{\text{Hg,outlet}}$ was the sum of Hg in flue gas, ashes and FGD slurry:

$$M_{\text{Hg,outlet}} = M_{\text{stack}} + M_{\text{fly-ash}} + M_{\text{bottom-ash}} + M_{\text{FGD-slurry}} \quad (3)$$

where, M_{stack} was the mass of Hg in the flue gas generated from a unit of coal measured at the stack. Based on the results from proximate and ultimate analyses of coal, the theoretical flue gas volume per kilogram coal can be calculated. The production rates (kg solid/kg coal) of bottom ash, fly ash, and FGD slurry were also determined by on-site operational data at the coal-fired power plant.

$M_{\text{Hg,inlet}}$ was the mass of Hg in the coal that was fed into the boiler when OHM sampling was running, and $M_{\text{Hg,inlet}}$ was calculated from the mercury concentration in the coal sample, and the calculation basis was per kg coal. By combining flue gas Hg data from the OHM testing results, the mass balance of Hg can be calculated and the results are summarized in Table 2. As shown in the table, the mass balance rates were from 0.84 to 1.08, and all the tests were

within the 20% acceptable ranges, which validates OHM mercury testing. In addition, higher percentage mercury was retained in the FGD slurry, but fly ash and bottom ash can capture insignificant mercury. The FGD slurry had a greater capability of in retaining mercury when SCR was in service. Therefore, the wet FGD system was an effective technology for controlling mercury emissions at coal-fired power plants.

3 Conclusions

Mercury measurements were conducted using air pollution control devices at a cyclone 190 MW boiler in the non-ozone and ozone seasons. Some conclusions were drawn including:

(1) Elemental mercury was the predominant mercury speciation from 74.0% to 98.0% when the SCR was not in service. The fraction of elemental mercury in the total mercury ranged 30.0% to 70.0% when the SCR was in service. Chlorine contents in coal affected mercury speciation at the SCR inlet. SCR was a key factor in oxidizing elemental mercury into oxidized mercury, with oxidation efficiency reaching 71.0%.

(2) Cold-side ESP can capture particulate mercury through fly ash. The fly ash characteristics including unburned carbon (UBC) and ash's basic chemical composition affected mercury removal through ESP. Mercury removal efficiencies ranged from 2.61% to 5.83% in the non-ozone season, while mercury capture efficiencies varied from 7.91% to 15.1% in the ozone season.

(3) There were higher fractions of oxidized mercury in the total mercury found in the flue gas, and oxidized mercury was water-soluble and dissolved in the wet FGD. Oxidized mercury was effectively removed through wet FGD. Between 54.9% and 68.8% of the total mercury was captured through wet FGD without SCR, but mercury removal efficiencies ranged from 78.0% to 90.2% with SCR system. Wet FGD was regarded as a near-term and co-benefit mercury control technology at coal-fired power plants.

(4) Mercury mass balance was evaluated to validate OHM testing, with mass balance rates varying between 0.84 and 1.08. All the tests were within the 20% acceptable ranges. Although a higher percentage of mercury was retained in the FGD slurry, fly ash and bottom ash can capture insignificant amounts of mercury.

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