Emission and Partitioning of Mercury at Various Combustion Sources

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Abstract: - While some advanced countries have paid much attention on mercury emission and it's hazard with regulating major anthropogenic sources, Korea has not been concerning on mercury issues until recent years. The first attempt to develop the emission inventory from major sources of mercury such as coal power plants and incinerators was made by the authors' team with Korean Ministry of Environment. At the same time several research organizations including Korea Electric Power Research Institute have made to investigate the status of emission and related control technologies. Very brief inventory data have been obtained so far with their speciation and behaviour to understand the effectiveness of existing air pollution control devices to handle mercury in the processes. The paper will deal with the emission characteristics of mercury from Korean combustion facilities which are coal power plants, waste incinerators and cement kilns with showing speciation changes and mass distribution of mercury in each plant.

Key-Words: - Mercury, Partitioning, Speciation, Coal power plants, Incinerators, Removal Efficiency.

1. Introduction

Coal naturally contains mercury and other chemical elements, which are different from type of coal and place of the origin, typically, mercury content in coal ranges from 0.01 to 0.48mg/kg. Mercury emission from such combustion systems occurs when mercury vaporizes during combustion and is exhausted through the combustor stack. There are numerous sources of mercury in wastes. These include electric switches and lighting components, paint residues and thermometers. The same USEPA report[1] described that around 87% of mercury is emitted from such combustion activities. Major chemical forms of mercury from combustion sources are oxidized mercury (Hg^{+2}) and elemental mercury (Hg^0). Another form could be Hg_p, particulate form of mercury, which is the portion of mercury being deposited into fine particles (dusts). Hg^{+2} species, such as $HgCl_2$, HgO, are easily removed by existing wet type air pollution control devices (APCDs) like flue gas desulfurization (FGD), due to its water-soluble property. Also Hg_p is removed with particle by main dust removal control devices such as electrostatic precipitators (ESP), bag filters, etc. On the other hand, Hg^0 is difficult to control because of its insolubility in water. Therefore the change of mercury speciation by converting or transferring each other is important to select the mercury control technologies and to understand the fate and behavior of mercury from combustion processes. Activated carbons, fly ash or dedicated sorbent injection methods at the upstream of particulate control devices were widely carried out in pilot scale or field experiments to demonstrate the mercury removal efficiencies. The results showed that specially treated activated carbons and some typical fly ash have affinity for mercury compounds, which can remove mercury or have a function to oxidize as an easily removal form of mercury (Hg^{2+}). Consequently, high mercury removal efficiencies can be expected through ESP or wet type FGD because Hg^{2+} is easier to remove than Hg^0. However, the total removal efficiency and mercury speciation quite depend on lots of operating condition such as type of coal, flue gas temperature and components, APCDs configuration and so on.

In this paper, mercury emissions from various stationary combustion sources such as coal-fired power plants, oil-fired power plants, industrial utility oil boilers, iron manufacturing plants, and industrial waste incinerators in Korea, were measured. The fate of Hg in a coal-fired power plant, including its removal

by APCDs was quantified by collecting and analyzing gaseous samples as well as solid and liquid samples such as fuel coal, fly ash from hopper, gypsum (by-product from FGD), lime or limestone, and effluents. The assessment of mercury emission and total mercury mass balance from a coal-fired power plant were estimated by gathered sample data.

2. Experimental

Coal-fired power plants, oil-fired power plants, industrial utility oil boilers, iron manufacturing plants, and waste incinerators were selected to measure mercury concentrations mainly at stacks as well as some points between the units of APCD. Table 1 shows the facilities tested. The gaseous sampling was implemented in accordance with Ontario Hydro method and US EPA 101A method that is based on Korean standard method.

Table 1. Facilities tested to measure mercury and number of experiment carried out

Combustion Source	Type	Number of experiment
Industrial Oil Boilers	Oil Boilers	2
	Oil Power Plant	1
Coal Power Plants	Anthracite	2
	Bituminous Coal	6
Steel Manufacturing Plants	Electric	2
	Sintering Furnace	1
Waste Incinerators	Industrial Waste combustor	5
	Municipal Waste combustor	5
	Cement Kiln	3
Total	9 Type of Combustion Source	27

3. Results and Discussion

3.1 Mercury Emission from Various Combustion Sources

The results of mercury emission measurements from selected combustion sources, total of 27 tests, are shown in Table 2. At the stacks of the Industrial Oil-fired Boilers (#1 and #2), total mercury emission concentrations ranged from 0.08 to 0.25 $\mu g/m^3$. Concentrations of total mercury measured at Oil-fired Power Plant were found to be 0.24-1.45 $\mu g/m^3$ at the inlet of the electrostatic precipitator (ESP) and 0.20-0.21 $\mu g/m^3$ at the stack. The lowest concentration for the total mercury emitted in this work agreed well with the value reported previously by the U.S. EPA. Oil consuming combustor gave the lowest mercury concentration while the industrial waste incinerator gave the highest value.

For the coal-fired power plants tested, the types of coal and APCDs were the major factors affecting the level of total mercury emission concentration before and after the APCDs, respectively. The anthracite coal-burning facilities emitted higher concentration of total mercury than that of the bituminous coal-fired boilers. Emission concentrations of Hg both at the inlet of the APCDs and out of the stack were very sensitive to the following factors: coal characteristics, APCDs' momentary condition, the variation of incoming mercury amounts, and flue gas temperature. In addition, fly ash may continuously adsorb and desorb Hg from and back into the flue gas depending on the momentary flue gas temperature.

There are two major types of furnace used for iron manufacturing plants; electric and sintering. In the case of an electric furnace, the Hg concentrations ranged from 0.69 to 8.58 $\mu g/m^3$ at the inlet of the filter bag and from 0.75 to 13.7 $\mu g/m^3$ at stack. For the sintering-furnace iron manufacturing plant, 13.27-14.05 $\mu g/m^3$ of Hg was measured at the inlet of the ESP and 10.18-19.12 $\mu g/m^3$ was measured at the stack. The variation in Hg emissions from iron manufacturing plants was due to the intermittent operating condition of melting processes.

The highest Hg emission value was recorded at the industrial waste incinerator due to the high mercury contents in industrial

hazardous wastes and the ranges of Hg concentration were quite broad. Fluctuation of the industrial waste characteristics (non-homogeneity) fed into the furnace resulted in the fluctuation in effluent Hg concentration. For Industrial Waste Incinerator #1, the mercury emission ranged in 619.23-1,318.14 $\mu g/m^3$ at the inlet of wet type particulate control device and 40.72-325.65 $\mu g/m^3$ at the stack. Industrial Waste Incinerators #2 and #3 with dry- and semidry-type APCDs (scrubber + bag filter) emitted mercury in the range of 14.27-59.26 $\mu g/m^3$ at the inlet of APCDs and 17.80-58.76 $\mu g/m^3$ at the stack. A Hg removal efficiency was calculated based on the ratio of concentrations at the inlet of APCDs and at the stack. The results show that industrial waste incinerator with a wet-type APCDs (Industrial Waste Incinerator #1) has achieved 85.6% Hg removal efficiency while incinerators with dry- or semidry-type APCDs (Industrial Waste Incinerators #2 and #3) have achieved only 21.1% and 9.6%, respectively. These results indicate that oxidized form of Hg (by strong oxidizer such as HCl and SO_x) is predominant in the incinerator flue gas, which can be readily removed in the wet-type scrubber due to its high solubility in an acidic solution [2,3].

Table 2. Results of mercury emission measurements from selected combustion sources

Combustion Source	Emission Conc. ($\mu g/Sm^3$)		Type of APCDs	Description
	Inlet of the APCDs	At the Stack		
Industrial Oil-fired Boiler #1	N.A.	0.21-0.25 (Avg. 0.23)	Multi Cyclone	Bunker B
Industrial Oil-fired Boiler #2	N.A.	0.08-0.16 (Avg. 0.13)	Multi Cyclone	Bunker C
Oil-fired Power Plant	0.24-1.45 (Avg. 0.65)	0.20-0.21 (Avg. 0.21)	ESP	Bunker C
Coal-fired Power Plant #1	10.44-37.77 (Avg. 23.45)	3.93-31.99 (Avg. 13.66)	ESP	Anthracite
Coal-fired Power Plant #2	1.30-5.41 (Avg. 1.78)	2.03-4.39 (Avg. 3.21)	ESP + FGD	Bituminous (imported)
Coal-fired Power Plant #3	1.01-5.41 (Avg. 3.66)	2.11-2.41 (Avg. 2.25)	ESP + FGD	Bituminous (imported)
Iron Manufacturing Plant #1	0.69-4.20 (Avg. 2.04)	5.05-13.70 (Avg. 9.72)	Bag filter	Electric Furnace
Iron Manufacturing Plant #2	6.47-8.58 (Avg. 7.29)	0.75-1.04 (Avg. 0.99)	Bag filter	Electric Furnace
Iron Manufacturing Plant #3	13.27-14.05 (Avg. 13.66)	10.18-19.12 (Avg. 14.66)	ESP	Sintering Furnace
Industrial Waste Incinerator #1	619.23-1318.14 (Avg. 968.68)	40.72-325.65 (Avg. 139.07)	Cooling Chamber + Cyclone + Spray Tower + Wet ESP	Industrial Hazardous Waste
Industrial Waste Incinerator #2	56.27-59.26 (Avg. 57.77)	23.69-58.76 (Avg. 45.57)	Dry Scrubber + Bag Filter	Industrial Hazardous Waste
Industrial Waste Incinerator #3	14.27-34.77 (Avg. 23.51)	17.80-24.71 (Avg. 21.25)	Semidry Scrubber + Bag Filter	Industrial Hazardous Waste

3.2 Variation of mercury concentration across APCDs in a Coal-fired Power Plant

Table 3 indicates mercury emission concentrations across APCDs and facility operating conditions that contain flue gas temperature, components and coal type. Mercury concentration was decreased through APCDs. At the up stream of ESP, the averaged mercury emission ranged from 2.63 to 2.79 □ /Nm^3 and that at down stream of ESP was 1.77~ 1.84 □ /Nm^3. Approximately 34% of mercury was reduced across ESP that caused by removal of fly ash in the flue gas. Generally, fly ash has affinity to mercury compounds which is likely to adsorb on the surface of fly ash because some kind of oxidized mercury like as $HgCl_2$ has sticky properties[4]; however, note that the ability of mercury removal can be affected by types of coal, flue gas composition as well as carbon contents in fly ash [1].

Table 3. Results of mercury emission across APCDs and operating conditions at a CPP.

Points	Method	Total Hg Conc.(□/Nm^3)		Flue gas Temp.(□)
		Average	S. D.	
Before ESP	Ontario	2.63(1.77~3.00)	0.58	123~146
	101A	2.79(2.62~2.89)	0.11	
After ESP	Ontario	1.77(1.25~2.25)	0.45	136~140
	101A	1.84(1.16~2.50)	0.73	
Stack	Ontario	1.69(1.04~2.41)	0.67	92~96
	101A	1.66(1.07~2.26)	0.66	
Stack(ICR)	Ontario	2.57	1.80	-
* ICR data : US EPA, Information Collection Request, 1999 * Coal type : Imported Bit. Blend Coal (ICR : Bit Coal fired plant)				

Final emission to the atmosphere from stack was about 1.66~1.69 □/m^3, which was small amounts of mercury due to removal of oxidized mercury through wet FGD. It can be explained that some oxidized mercury could be absorbed by lime-slurry when mixing in the FGD scrubber tower because of its water-soluble property. However, many of researchers have studied that the role of wet FGD for mercury removal and speciation. The results indicate that some oxidized mercury could be removed in wet slurry as well as reduced in the scrubber solution through chemical reaction [5], then Hg^0 re-entrained into the wet FGD outlet flow. Therefore, the total mercury concentration and portion of Hg^0 in the flue gas were occasionally higher than those of inlet [6]. Overall mercury removal efficiency was about 33~40% across ESP and wet FGD that agree with previous US EPA results, which Hg removal efficiencies ranged 29~74 % according to coal type [1]. Previous studies indicate that NOx reduction system can affect the mercury speciation that increased the oxidation of Hg^0. Therefore, if coal-fired boilers equipped with SCR, ESP, and wet FGD, the highest mercury removal efficiency could be expected [7,8].

3.3 Mass Distribution of Mercury in a Coal-fired Power Plant

Mercury mass balance was calculated from the results of entire sample analysis at coal fire power plants and incinerators. To calculate the mass partitioning at a power plant, the weights of in and out of mercury were calculated from the results of measurement of mercury in fuel, residues sampled and gas streams. The recovery was about 93% in this case. Similar calculations were made to get the mass partitioning of mercury at other facilities such as coal power plants and incinerators. Fig 1-3 show the mass partitioning results at various plants tested in this study. For bituminous coal power plants, based on three different experiments, it indicates that approximately 61 % of Hg is collected in ESP fly ash hopper and 21.1 % of Hg is released into atmosphere,

8.7% of Hg remains in the gypsum, 1.3 % is collected in bottom ash. Those results well agree with previous study except fly ash content (in ESP hopper) and gypsum. It supposed that the difference of coal type and operating conditions could affect Hg speciation, according to the coal composition such as chlorine and sulfur the mercury oxidation and speciation might be changed in the combustion condition. Therefore, to understand exact fate and behavior of mercury from coal-fired power plants, long-term experiment plan and monitoring the flue gas are required continuously. Fig.2 shows the mass balance results for two different APCD configurations at MWIs. Most of Hg was captured by fly ash due to tight APCD units to control other pollutants such as dioxins and acidic gases. In case of wet type of APCD equipped MWI facility showed less capture of Hg by APCDs.

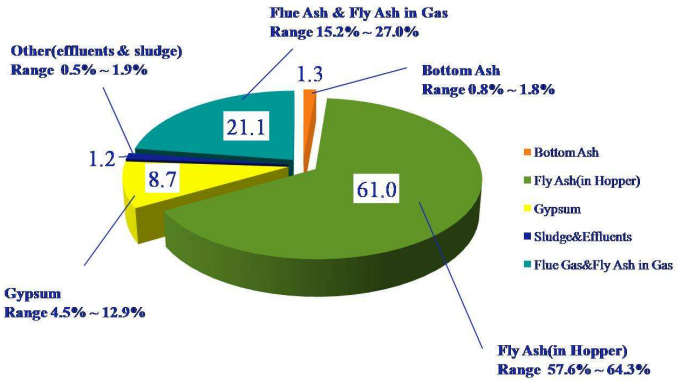
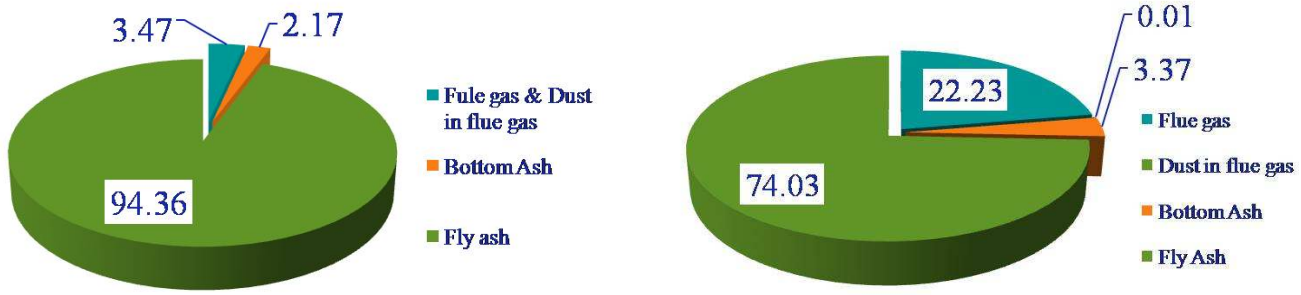
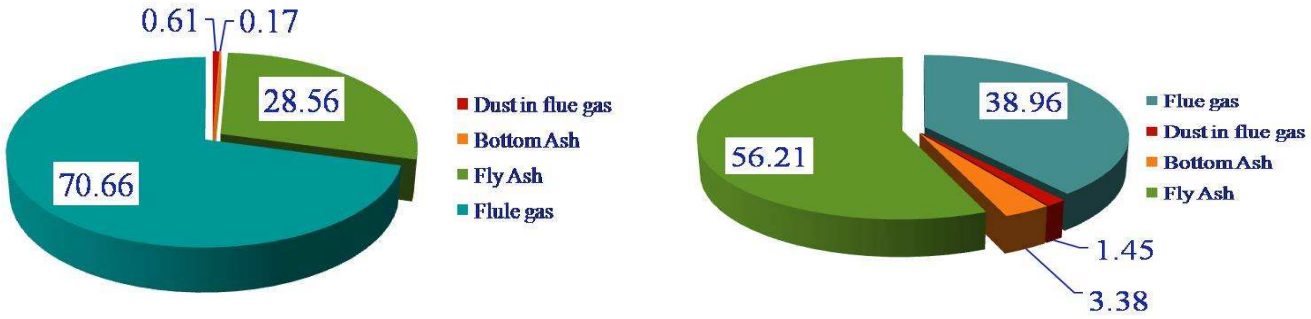


Fig. 1 Mass Partitioning of Hg in Bituminous-Fired Power Plants



(a) (b)

Fig. 2. Mass Partitioning of Hg in MSW Incineration Plants with Different APCD Types; (a) dry type (b) wet type



(a) (b)

Fig. 3 Mass Partitioning of Hg in Two different ISW Incineration Plants with Different APCD Types; (a) dry type (b) wet type

4. Conclusion

To investigate the Hg emission characteristics from stationary combustion sources in Korea, Hg sampling was carried out at 27 selected combustion facilities. It was found that the Hg emission was dependent on fuel type, APCDs configuration, and flue gas condition. The lowest Hg concentration was obtained from an oil consuming combustor while the highest value was recorded at the industrial incinerator. Type of coal was a major factor characterizing the Hg emission from coal-fired utility boilers; anthracite coal with a higher concentration of Hg emitted than bituminous coal. Understanding that the emission characteristics are very source-dependent and source-specific, flue gas speciation results in this study showed that larger portion of Hg^0 was found in coal-fired utility boilers while Hg (II) was dominant at industrial waste incinerators.

A good total mercury mass balance was obtained with about 90% recovery in this study, which was enough to describe the distribution of mercury in the plant. The distribution of mercury showed the highest portion of release with ESP ash and significant amount of removal by FGD operation, which indicated the effect of APCDs removal of dusts on the mercury reduction. And about a quarter of mercury still emitted into the atmosphere through stack. In case of MWIs, most mercury seemed to be remained in fly ash due to efficient APCDs to remove other gaseous pollutants. The mass partitioning of mercury at IWIs, however, showed site-specific results with dominant portion of release to atmosphere sometimes.

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