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# Studies on Speciation Changes and Mass Distribution of Mercury in a Bituminous Coal-Fired Power Plant by Combining Field Data and Chemical Equilibrium Calculation

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Transformation of mercury compounds in combustion flue gas and overall mercury mass balance in a typical bituminous coal-fired power plant were studied. Upon decreasing temperature and interaction with flue gas components, oxidized mercury increased across an electrostatic precipitator. A major fraction of particulate mercury was removed in the electrostatic precipitator, and oxidized mercury was removed in wet flue gas desulfurization. Hg was mainly speciated into elemental form in the stack emission. The measurement of mercury in a real facility and equilibrium calculation showed that coal composition, operating conditions, and flue gas components were the major factors affecting mercury emission and speciation. A reliable overall Hg mass balance was obtained from the field measurement. Mercury mainly entered from coal, and lime/limestone feeding was distributed in electrostatic precipitator fly ash (57.6–64.3%), gypsum (4.5–12.9%), effluents (0.5–1.9%), and stack emission (15.2–27.0%). Further, the mass distribution and speciation of mercury in the power plant with simulated coal mixture feeds could be predicted with a chemical equilibrium code in combination with the measured results at the commercial plant.

## 1. Introduction

Mercury (Hg) is a toxic, global air pollutant. Worldwide, anthropogenic combustion facilities are the major sources emitting Hg into the atmosphere. Coal-fired power plants are the largest anthropogenic sources of unintentional Hg release into the atmosphere.<sup>1</sup> In Korea, study on Hg emission behavior from anthropogenic sources has been accelerated in the recent past, and coal-fired power plants have been recognized as one of the major sources of Hg emission.<sup>2–4</sup>

In 2005, the U.S. EPA issued a clean air mercury rule (CAMR),<sup>5</sup> which uses a cap-and-trade approach to reduce Hg emission in two separate phases. A first-phase cap of 38 tons/year becomes effective in 2010, and a second phase cap of 15 tons/year becomes effective in 2018. CAMR aims to reduce Hg emission from coal-fired power plants approximately by 70% of the Hg emission in 1999. Unfortunately, in February 2008, the CAMR was vacated by the district court of appeals. Now the U.S. EPA must either follow up in a higher court or promulgate a new regulation.<sup>6</sup> In February 2009, more than 140 countries agreed to negotiate a legally binding treaty to reduce the use of the metal Hg.

To meet stringent regulatory requirements, several research studies on technical and regulatory control of Hg from coal-fired power plants have been carried out. Before technical and regulatory control are applied, understanding Hg behavior in combustion sources and within air pollution control devices (APCDs) is essential. Hg compounds can be controlled by existing APCDs installed to control particulates, NO<sub>x</sub>, and SO<sub>x</sub> as a cobenefit control. Hg in combustion flue gas is speciated in three forms: oxidized (Hg<sup>2+</sup>), elemental (Hg<sup>0</sup>), and particle-bound (Hg<sub>p</sub>). Hg<sup>0</sup> is difficult to control because it is insoluble in water, usually escapes emission control equipment, and finally is emitted into the atmosphere. Hg<sub>p</sub> can be removed in particulate control devices. Hg<sup>2+</sup> is soluble in water and can be removed in wet scrubbers. Hg speciation and oxidation in

flue gas varies with flue gas composition and APCDs type. Studies do suggest that coal sulfur, chlorine, and mercury concentrations influence Hg emission during combustion.<sup>7,8</sup> Similarly, flue gas components SO<sub>3</sub>,<sup>9,10</sup> Cl and HCl,<sup>11,12</sup> and NO,<sup>13</sup> among others, are reported to influence Hg oxidation in flue gas. Thus, understanding Hg speciation and oxidation behavior in flue gas is important to effectively control Hg emission from coal-fired power plants.

Hg introduced into the power plants via coal and limestone undergoes transformation and removal within APCDs, and the remaining is emitted into the atmosphere through the stack. Hg mass balances study in a coal-fired power plant give a clear picture of Hg distribution in different streams. Further, it provides an important clue for applying control technology. However, Hg mass balance and distribution study in the industrial facilities, for instance, in a coal-fired power plant is a difficult task due to the labor, time, and the cost associated with it. Because of these reasons, predicting Hg emission, speciation, and mass distribution in a coal-fired power plant using a chemical equilibrium program in combination with real measurements has a broad implication. This approach of Hg prediction saves labor, time, and money. In this paper, first the emission and speciation variations of Hg in flue gas within APCDs were measured at a coal-fired power plant. With detailed input and output analysis, Hg mass balance at a plant was estimated. Computer simulation code, chemical equilibrium with analysis (CEA) code,<sup>14</sup> was used to predict Hg emission at different coal compositions and operating conditions. Further, mass distribution of Hg at different scenarios was predicted using the program with information from real measurement data.

## 2. Methodology

The typical coal-fired power plant in Korea was selected for studying Hg speciation transformation in flue gas and Hg mass distribution in a whole system. The tested plant combusted pulverized, blended bituminous coal. The plant tested had 500 MW boilers. The cold-side electrostatic precipitator (ESP) and

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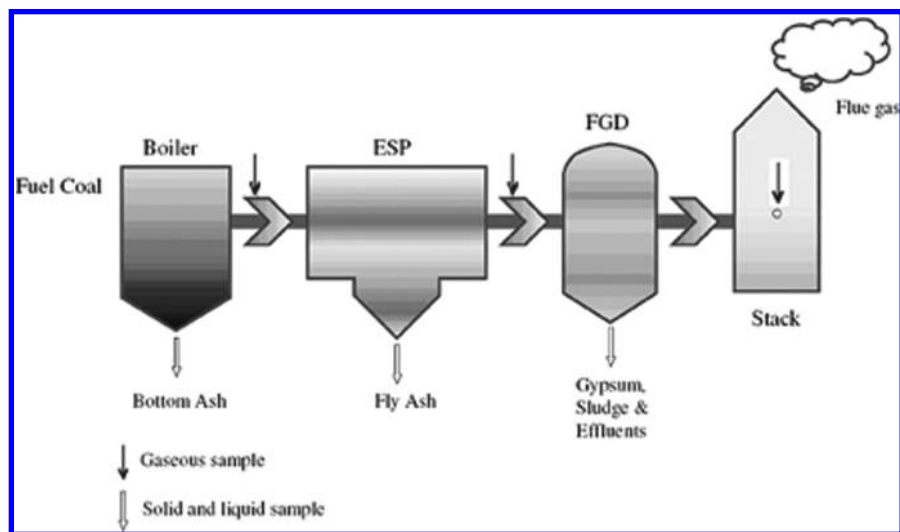


Figure 1. Schematic diagram of a coal-fired power plant.

Table 1. Properties of Major Coals Used in Korean Power Plants

coal	proximate analysis (%)				elemental analysis (%)						Hg (mg/kg)	Cl (mg/kg)	heating value (kcal/kg)
	moisture	volatile	fixed carbon	ash	H	C	N	S	O				
NCA (Australia)	2.97	19.99	58.46	18.58	5.12	49.9	1.16	4.25	18.1	0.068	628.4	6227.05	
Sanseo (China)	7.73	26.95	52.19	13.14	4.40	56	0.89	9.11	8.74	0.068	263.04	6423.9	
Shinwha (China)	9.00	31.35	54.28	5.38	5.35	56.9	0.81	5.57	17	0.049	130.38	6709.65	
B.A (Indonesia)	13.23	25.17	53.79	7.81	3.94	57.7	1.14	6.43	9.79	0.051	263.04	6626.45	
Rotosouth (Indonesia)	19.79	41.77	36.49	1.95	5.43	60.5	0.20	1.19	11.0	0.062	30.04	5686.55	
Fording (Canada)	2.47	22.99	60.38	14.16	3.33	48.9	0.73	12.3	18.2	0.039	104.28	6683.0	
Indominco (Indonesia)	10.23	41.01	46.00	2.76	4.88	58.3	1.20	3.29	19.4	0.024	7.09	6237.4	
Kuzbass (Russia)	3.97	24.50	57.87	13.65	3.49	43.8	0.64	2.93	31.5	0.053	16.17	6371.15	
Ensham (Indonesia)	4.80	24.7	59.28	11.22	3.53	46.9	0.94	3.27	29.3	0.012	594.14	6711.3	
KPC (Indonesia)	10.22	41.05	45.48	3.24	4.52	54.2	1.10	2.45	24.2	0.032	37.75	6149.4	
anthracite (domestic)	1.58	6.17	65.40	26.85	0.58	32.1	0.40	3.24	35.2	0.297	20.61	5168.8	

wet flue gas desulfurization (FGD) were installed for particulate and  $\text{SO}_x$  removal, respectively. A schematic diagram of the selected power plant is shown in Figure 1.

Hg speciation in the flue gas was sampled and analyzed by Ontario Hydro method. Solid and liquid samples were analyzed by U.S. EPA methods 7470A and 7471A, respectively. A cold vapor atomic absorption spectroscopy (CVAAS) Hg analyzer (RA+915, Lumex) was used for analysis. Coal elemental analysis (C, H, N, O, and S) was done by adopting ASTM D 3176 standard practice for ultimate analysis of coal and coke.

A total of 10 imported bituminous and one domestic anthracite coals, used in commercial power plants, was considered for analysis. The elemental content (H, C, N, S, and O), Hg and chlorine concentrations, and the heating value of the coals were measured. Hg concentrations in each ingoing stream (coal and lime/limestone) and outgoing stream (bottom ash, fly ash in ESP hopper, gypsum, FGD effluents, and flue gas) were measured. Coal was sampled from the coal feeding, the bottom ash from the boiler, the fly ash from the ESP hopper, the gypsum, and the effluents from FGD. The sampling and measurement of Hg and its speciation in the flue gas, at the inlet and outlet of each APCD, were carried out. The flue gas, solid, and liquid sampling points are marked in Figure 1. Solid and liquid samples were collected simultaneously from the facility during emission tests. Using the Hg concentration and the flow rate at each ingoing and outgoing stream, the mass concentration was estimated. Mass distributions within the system and the in/out balance of Hg in the whole system were estimated. A computer simulation program, CEA code, was used to predict Hg emission and speciation in the flue gas at the boiler outlet, on the basis of the coal elemental composition including

the Hg concentration. With the information from real measurement data the mass distribution of Hg at different scenarios was also predicted. Two coals with the highest (NCA) and the lowest (Ensham) Hg concentrations are considered for emission prediction by the CEA code, while Hg emission concentration measurements at the facility are reported only for one coal blend.

### 3. Results and Discussion

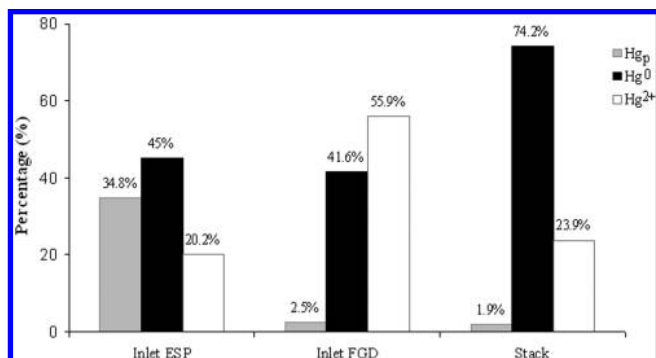
**3.1. Coal Properties.** Coal property is an important parameter for Hg emission and speciation during coal combustion in a power plant. The summary of proximate and ultimate analysis of coal samples used in Korean power plants is shown in Table 1. Mean values of Hg and chlorine concentrations and heating values are also summarized. Analysis of one of the domestic anthracite coals is also presented for comparison. The elemental content in coal ranged for C from 43.8 to 60.5%, for S from 1.19 to 9.11%, for H from 3.33 to 5.43%, for N from 0.2 to 1.16%, and for O from 8.7 to 31.5%. In bituminous coal samples, moisture content ranged from 2.47 to 19.79%, volatile matter from 19.99 to 41.77%, fixed carbon from 36.49 to 60.38%, and ash from 1.95 to 18.58%. The heating values of the bituminous coal samples ranged from 5686.5 to 6711.3 kcal/kg. The chlorine concentration in the coal ranged from 7.09 to 628 mg/kg.

Hg emission into the atmosphere from coal combustion is directly related to its content in the coal. Coal contains a trace amount of Hg, which differs with the place of origin, formation, types, and sulfide content, etc. Hg content in the bituminous coals varied from 0.012 to 0.068 mg/kg with an average value of 0.046 mg/kg. The higher concentrations were found in NCA

**Table 2. Mercury Emission and Speciation Variation across APCDs<sup>a</sup>**

Hg speciation	inlet ESP		inlet FGD		stack	
	$\mu\text{g}/\text{Nm}^3$	%	$\mu\text{g}/\text{Nm}^3$	%	$\mu\text{g}/\text{Nm}^3$	%
Hg <sub>p</sub>	0.93	34.8	0.04	2.5	0.03	1.9
Hg <sup>0</sup>	1.20	45.0	0.67	41.6	1.18	74.2
Hg <sup>2+</sup>	0.54	20.2	0.90	55.9	0.38	23.9
total Hg	2.67	100	1.61	100	1.59	100

<sup>a</sup> An average value of the several tests at the identical condition using the same mixed coal is presented.



**Figure 2.** Mercury speciation variations across APCDs of coal-fired power plant. Average of the several tests carried out in a power plant.

and Sanseo coals (0.068 mg/kg), whereas there was a lower concentration of 0.012 mg/kg in the Ensham coal. The Hg content in the domestic anthracite coal was 0.297 mg/kg, which is several times higher than that of the bituminous coal. Bituminous coals used in Korean power plants are imported from foreign countries. Thus, a wide variation in coal Hg content was measured. The literature shows a wide range of variations in the average Hg content in coals, varying from 0.02 to 1 mg/kg.<sup>15,16</sup> An average of 0.10 mg/kg of Hg was contained in coal supplied to U.S. power plants in 1999.<sup>7</sup> Coal composition data in Table 1 are used to predict Hg emission during coal combustion, using a computer simulation program.

### 3.2. Hg Behavior across Air Pollution Control Devices.

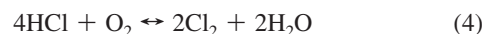
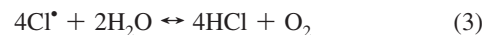
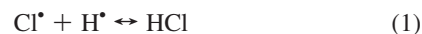
Table 2 and Figure 2 show Hg speciation variation and transformation, averages of several tests at the outlet boiler/inlet ESP, the outlet ESP/inlet FGD, and the outlet FGD/stack. When flue gas passes through a cleaning system, a portion of the Hg is removed at each APCD; thus, the measured Hg concentration decreased across each APCD. Hg emission concentrations at the boiler outlet and the stack emission of the tested power plant were 2.67 and 1.59  $\mu\text{g}/(\text{N m}^3)$ , respectively. The experimental data revealed lower Hg emission concentration at the boiler outlet, which could be due to the use of mixed coal with lower Hg content. Similar Hg emission concentrations from stacks of coal-fired power plants have also been reported.<sup>3,17</sup> Overall the Hg control efficiency of APCDs (ESP and wet FGD) was 40.5%. This is similar to data from a previous U.S. EPA report, where Hg removal efficiencies ranging from 29 to 74% are reported, which differed depending on the coal types and the APCDs in operation.<sup>18</sup> Here it is important to note that Hg removal in APCDs depends on various factors such as coal composition, coal chlorine content, Hg speciation, operating conditions, and flue gas components, etc.

**3.2.1. Hg Behavior in ESP and Effect of Flue Gas Components.** In the combustion zone of a boiler, Hg in coal vaporizes and is converted mainly into thermodynamically stable Hg<sup>0</sup>. As the flue gas passes the cleaning systems, the temperature decreases and Hg<sup>0</sup> undergoes several reactions, transforming into Hg<sup>2+</sup> and Hg<sub>p</sub>. Hg<sub>p</sub> is removed in the ESP, but the gas-

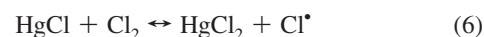
phase Hg is not; however, Hg<sup>0</sup> can be transformed into Hg<sup>2+</sup> and Hg<sub>p</sub>. Our field test results showed that at the ESP inlet a higher portion of Hg was distributed in Hg<sup>0</sup> followed by Hg<sub>p</sub> and Hg<sup>2+</sup>. In the ESP 95.7% of Hg<sub>p</sub> was removed along with particulate removal. The share of Hg<sup>2+</sup> increased passing through ESP; i.e., more Hg<sup>2+</sup> (55.9%) was formed than Hg<sup>0</sup> (41.6%). This is due to the conversion of Hg<sup>0</sup> into Hg<sup>2+</sup> upon decreasing temperature and interaction with the flue gas components. Oxidation of Hg<sup>0</sup> across the ESP has also been reported by previous research.<sup>19,20</sup> The literature supports that Hg in combustion flue gas undergoes homogeneous and heterogeneous oxidation,<sup>21,22</sup> forming oxidized Hg species. The degree of conversion of Hg<sup>0</sup> to Hg<sup>2+</sup> and Hg<sub>p</sub> primarily depends on the flue gas components, operating conditions, process configuration, quenching rate, and APCDs configuration, etc.

In our field test 34.8% of Hg<sub>p</sub> was observed at the outlet of a boiler. It is likely that fly ash contained more unburned carbon, providing more sites for Hg sorption, resulting in higher amounts of Hg<sub>p</sub>. Activated carbon and fly ash is an important parameter for Hg sorption, which contains active carbon sites where Hg can bind, as explained in other literature.<sup>22–24</sup> On the other hand, sulfur oxides such as SO<sub>2</sub> and SO<sub>3</sub> can bind to these active sites, inhibiting the binding of Hg.<sup>9</sup> Thus, sorption and desorption of Hg in fly ash is bit complex, which depends on flue gas condition and interaction with several species. Hg oxidation in the flue gas is mainly caused by halogen species (mainly bromine and chlorine), acid gases (SO<sub>x</sub>, NO<sub>x</sub>, and HCl), and O<sub>2</sub>. The effect of coal properties and flue gas components on Hg oxidation will be discussed in the following sections.

**(a) Effect of Chlorine.** The distribution of mercury species in combustion flue gas depends upon the coal's chlorine concentration. A higher portion of Hg is speciated into Hg<sup>2+</sup> in flue gas when the combusted coal has a high chlorine concentration. For this reason, chlorine content in coal is an important parameter to consider. The chlorine concentration in the tested coals used in Korean power plants ranged from 7.09 to 628.40 mg/kg. Bituminous coals, in general, contain higher chlorine concentrations, ranging from 500 to 1300 mg/kg, with HCl in the flue gas ranging from 50 to 130 ppmv.<sup>11</sup> Due to higher Cl content in bituminous coal, the portion of Hg<sup>2+</sup> in the combustion flue gas is relatively higher. During combustion, the chlorine in coal is mainly released as atomic chlorine, which further forms HCl or Cl<sub>2</sub>, as shown in the following reactions.<sup>8,12</sup>



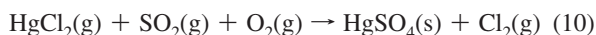
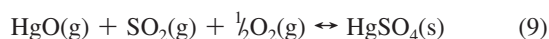
The reactivity of Hg<sup>0</sup> with Cl atom ( $1.0 \times 10^{-11} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ ) is higher than that with Cl<sub>2</sub> ( $2.6 \times 10^{-18} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ ).<sup>25</sup> Thus, the oxidation of Hg<sup>0</sup> by Cl atom is more favorable than by Cl<sub>2</sub>. Earlier literature reports that more Hg<sup>2+</sup> is formed at lower temperatures and at higher chlorine content in coal, as shown in reactions 5–8.<sup>8</sup> Further, the same study concluded that chlorine in flue gas was responsible for Hg oxidation and chemisorption on fly ash. However, high Cl concentration cannot always form high Hg<sup>2+</sup> concentration.<sup>26</sup>







(b) **Effect of S, SO<sub>2</sub>, and NO.** The sulfur content in coal and the SO<sub>2</sub> concentration in flue gas have an influential effect on Hg<sup>0</sup> oxidation in flue gas. With increasing coal S content, a decreasing tendency of Hg removal in power plants is reported.<sup>7</sup> S may inhibit the conversion of HCl to Cl<sub>2</sub> in flue gas and sulfation of catalytic metal oxide surfaces and promotes reduction of Cl to HCl, which is less reactive.<sup>27</sup> Frandsen et al.<sup>28</sup> proposed the following reaction to explain the involvement of S and Cl in Hg oxidation. Sulfur in coal and SO<sub>2</sub> in flue gas have been reported to promote Hg<sup>2+</sup> and decrease Hg<sup>0</sup> formation.<sup>8</sup>

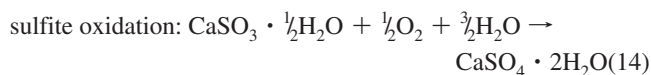
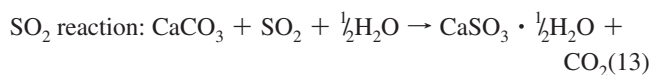


Agarwal et al.<sup>13</sup> presented H<sub>2</sub>O, SO<sub>2</sub>, and NO as having an inhibitory effect on homogeneous oxidation of Hg by Cl<sub>2</sub>. They proposed the reactions to explain the role of Cl<sub>2</sub>, NO, and SO<sub>2</sub> as shown in the reactions 11 and 12 as follows.



By all the reaction pathways and the discussions presented above, it is clear that Hg transformation and oxidation in coal combustion flue gas is nonlinear and complex. Further, Hg<sup>0</sup> oxidation in the flue gas depends on many factors acting simultaneously. Thus, it is hard to predict Hg speciation with certainty, considering its variations with operating conditions, coal types, and so on.

**3.2.2. Hg Behavior in Wet FGD.** In the wet FGD system an alkaline reagent, mostly lime or limestone, is injected into the flue gas to react with SO<sub>2</sub> and water, forming salt byproduct. Since Hg<sup>2+</sup> is water-soluble, it can simultaneously be removed in a scrubber solution. Hg removal in wet FGD depends on Hg speciation and the upstream APCDs configuration, etc. The fundamental chemical reactions in a wet FGD system with a limestone reagent are shown as follows.<sup>29</sup>



Removal and re-emission of Hg in wet FGD is one of the important parameters for studying Hg behavior in FGD. In the tested facility 57.7% of Hg<sup>2+</sup> was removed in wet FGD. At the same time, 31.7% of Hg<sup>0</sup> increased in the wet FGD scrubber

solution because of the re-emission of dissolved Hg<sup>2+</sup>. The increase in Hg<sup>0</sup> in the wet FGD system is due to the reduction of Hg<sup>2+</sup> absorbed in the scrubber solution to Hg<sup>0</sup>. Study<sup>30</sup> in a laboratory-scale wet scrubber found Hg<sup>2+</sup> can be reduced by S(IV), resulting in Hg<sup>0</sup> emission. Field test data<sup>29</sup> has reported reduction and re-emission of Hg<sup>2+</sup> in wet FGD scrubber solution as Hg<sup>0</sup>.

**3.2.3. Mercury in Stack Emission.** Hg entered into the power plant system undergoes several transformations and removal processes, and the remaining portion is eventually emitted into the atmosphere. The fate of Hg in the environment depends on its speciation in the emission gas. Hg<sup>2+</sup> and Hg<sub>p</sub> tend to settle near the emission sources, while Hg<sup>0</sup> is unreactive and can reach far distance from the sources. Thus, knowing the Hg speciation in emission gas is important. In stack emission 74.2, 23.9, and 1.9% of Hg on average were distributed to Hg<sup>0</sup>, Hg<sup>2+</sup>, and Hg<sub>p</sub>, respectively. The coal types, APCDs configuration, operating conditions, and temperature were the major factors affecting Hg emission and speciation at the stack. Many researchers<sup>3,11</sup> reported such behavior, and it was confirmed in our measurements as well.

**3.3. Mass Balance of Mercury in a Coal-Fired Power Plant.** Hg entered into the power plant from coal and limestone feeding is removed through several streams: boiler bottom ash, fly ash (ESP), FGD byproducts (gypsum, sludge, and effluents), and stack emission. Measurements of the coal and lime/limestone feed rate, fly ash, sludge, and effluent generation rate during the emission test were undertaken for the mass balance study. With the measured Hg concentration and flow rates at each ingoing and outgoing stream, Hg mass distributions were estimated. With several tests at identical conditions the average Hg input and output rates were estimated, as summarized in Table 3.

On average, 99.8% of Hg entered into the coal-fired power plant system from coal feeding and 0.2% from lime/limestone injection. The average Hg mass concentrations entering the boiler from coal feeding and lime/limestone injection were 12.21 and 0.02 g/h, respectively, while, in the removal stream, 7.62 g/h of Hg was removed in the fly ash of the ESP hopper. Also, 1.54 g/h of Hg was removed in gypsum and 0.23 g/h in sludge and effluent. A 0.22 g/h amount of Hg was removed in the boiler bottom ash. Gaseous and particulate Hg emission rates from the stack were 2.25 and 0.07 g/h, respectively.

The Hg mass balance was estimated by considering the sum of the Hg input from coal and lime/limestone as 100%. In the present study in/out Hg mass balance with about 97% recovery on average was obtained, which is adequate to explain the mass distribution in the different streams of the power plant. The mass

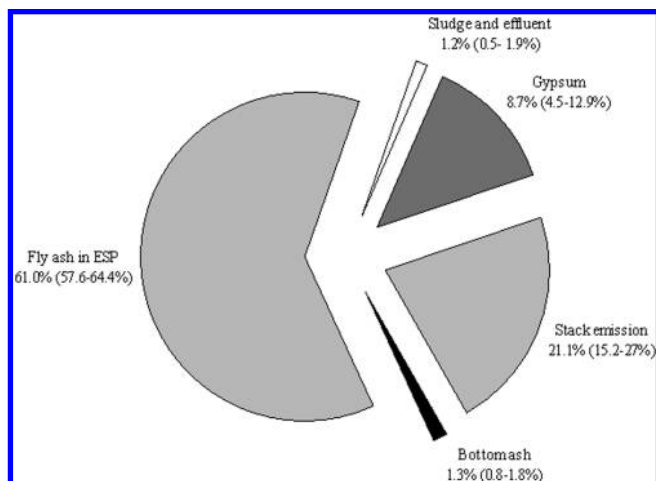
**Table 3. Mercury Mass Balance Estimation in a Power Plant<sup>a</sup>**

Hg mass flow rate and balance (%)	incoming			outgoing					
	total	coal	lime/limestone	total	fly ash (ESP)	flue gas and fly ash	gypsum	bottom ash	sludge and effluent
flow rate (g/h)	12.23	12.21 <sup>b</sup>	0.02 <sup>c</sup>	11.93	7.62 <sup>d</sup>	2.25 <sup>e</sup> and 0.07 <sup>f</sup>	1.54 <sup>g</sup>	0.22 <sup>h</sup>	0.23 <sup>i</sup>
mass balance (%)	100	99.8	0.2	97	63.9	18.9 and 0.006	12.9	1.8	1.9

<sup>a</sup> An average value of the several tests at the identical condition while combusting the same mixed coal is considered. <sup>b</sup> Average coal feed rate, 4128 tons/day. <sup>c</sup> Calculated on the basis of the gypsum generation rate including process water. <sup>d</sup> Average Hg in fly ash, 0.37 mg/kg. <sup>e</sup> Estimated flue gas flow rate, 1618860 N m<sup>3</sup>/h. <sup>f</sup> The average fly ash content was 2.8% of total emission in the stack. <sup>g</sup> Estimated gypsum generation rate, 137 tons/day. <sup>h</sup> Estimation based on coal ash content. <sup>i</sup> Including sludge and effluent from wet FGD.

**Table 4. Mercury Emission Calculation for Two Coals from a Combustor Using CEA Code**

coal	prediction by CEA code		conversion		Hg in flue gas (at boiler outlet)			
NCA	9.85 × 10 <sup>-10</sup> mol of Hg(g)	1 mol of gas	200.5 g	1000 L	10 <sup>6</sup> μg	8.81 μg/(N m <sup>3</sup> )		
	1 mol of gas	22.4 L	1 mol of Hg(g)	1 m <sup>3</sup>	1 g			
Ensham	2.43 × 10 <sup>-10</sup> mol of Hg(g)	1 mol of gas	200.5 g	1000 L	10 <sup>6</sup> μg	1.76 μg/(N m <sup>3</sup> )		
	1 mol of gas	22.4 L	1 mol of Hg(g)	1 m <sup>3</sup>	1 g			



**Figure 3.** Mercury distributions in coal-fired power plants. The range of distribution is presented in the bracket based on the mass balance study in three similar power plants.

distribution of Hg shows that 63.9% was collected in ESP fly ash removal, 14.8% of Hg was removed in FGD byproducts and effluents (12.9% removed in gypsum and 1.9% in sludge and effluents), and 1.8% of Hg was removed in the boiler bottom ash. Finally, the remaining 18.9% of Hg was released into the atmosphere from the stack (Table 3). With the Hg mass distribution study data, available at the laboratory, at three similar power plants, the distribution ranges at each stream were calculated as shown in Figure 3. Hg mass distribution indicated that 57.6–64.3% of Hg entering into the power plant was captured in ESP fly ash. In FGD gypsum 4.5–12.9% Hg was removed and 0.5–1.9% in FGD effluents; 0.8–1.8% of Hg was removed in the boiler bottom ash. Ultimately 15.2–27.0% Hg was released into the atmosphere. It is clearly observed that a higher portion of the Hg entering the system is distributed in the ESP fly ash. The Hg mass distribution in the present study is similar to those of the earlier studies by Lee et al.<sup>3</sup> and Park et al.<sup>31</sup> in Korea. Hg distribution behavior in the present study was also similar to typical Dutch coal-fired power plants with ESP and wet FGD.<sup>32</sup>

Currently, most of the power plants in Korea have installed an SCR system to meet the stringent NO<sub>x</sub> emission limit. Installation of an SCR system in coal-fired power plants is found to increase Hg oxidation and enhance overall removal in APCDs.<sup>4,33</sup> The Hg mass balance study in a power plant with an SCR system is under progress and will be disclosed in the future.

**3.4. Prediction of Mercury Emission and Distribution with CEA Code.** With elemental composition, including the Hg concentration, in coal, the chemical equilibrium products concentration of Hg at combustion condition can be estimated using a computer simulation program. The chemical equilibrium products of Hg emission concentrations at 1600 K (1327 °C) and the air/fuel ratio of 1.2 were predicted, as shown in Table 4. This condition is similar to real combustion conditions in coal-fired power plants. The predicted results were produced with a mole fraction of 1 mole of combustion gas, which was converted to Hg concentration in flue gas. Hg emission was predicted to be 8.81 μg/(N m<sup>3</sup>) from NCA coal and 1.76 μg/(N m<sup>3</sup>) from Ensham coal combustion, respectively. Hg emission concentrations measured at the real facility differed with that predicted by CEA code application for NCA and Ensham coal since the coal used at the tested plant was blended. However, Hg emission concentration (2.67 μg/(N m<sup>3</sup>)) measured at the

real facility lies within the predicted range of these two coals (1.76–8.81 μg/(N m<sup>3</sup>)).

Hg concentration at the inlet of the ESP was calculated using CEA code. Hg concentrations at the ESP outlet and stack were estimated using the mass balance information, as introduced in the previous sections. Hg speciations at each point were estimated using the real measurement data. By this approach, if we have elemental composition and Hg content in any mixed coals, Hg concentration and distribution can be estimated. The speciation distribution obtained from the real measurements can be applied to estimate the speciation in any similar plants under study. The mass distributions of Hg at two scenarios for combusting bituminous coals, while burning NCA and mixed coal (NCA and Ensham), are presented in the following section.

**3.4.1. NCA Coal.** The predicted Hg concentration and speciation at a coal-fired power plant, using NCA coal, is shown in Figure 4. NCA coal was one of the higher Hg-containing coals among those used in the Korean plants. The higher Hg emission concentration, 8.81 μg/(N m<sup>3</sup>) at the boiler outlet and 2.02 μg/(N m<sup>3</sup>) at the stack emission, were predicted. Among 8.81 μg/(N m<sup>3</sup>) of Hg released at the boiler outlet, 0.12 μg/(N m<sup>3</sup>) is removed in the boiler bottom ash and 8.78 μg/(N m<sup>3</sup>) is distributed into the flue gas. Out of 8.66 μg/(N m<sup>3</sup>) of Hg entering into the ESP, 5.65 μg/(N m<sup>3</sup>) is removed along with particulate removal and the remaining 3.02 μg/(N m<sup>3</sup>) enters into the wet FGD system, where 1.0 μg/(N m<sup>3</sup>) of Hg is removed along with gypsum, sludge, and effluents. Finally, the remaining 2.02 μg/(N m<sup>3</sup>) is predicted to emit into the atmosphere.

**3.4.2. NCA and Ensham Coal.** To predict Hg emission and the distribution scenario during blended coal combustion, the NCA and Ensham coal mixing ratio of 0.13:0.87 was considered, as an example. Hg emission after the boiler from mixed (NCA and Ensham) coal was 2.67 μg/Nm<sup>3</sup>, which is lower than the previous estimation with NCA coal. This mixing ratio produced a similar emission concentration with the measured data at the real plant. Similar to scenario I, Hg distributions at each point and each stream were predicted, as shown in Figure 5. At the outlet of the boiler, 2.67 μg/(N m<sup>3</sup>) of Hg emission was predicted, of which 0.03 μg/(N m<sup>3</sup>) can be expected to be removed in the boiler bottom ash, and 2.63 μg/(N m<sup>3</sup>) is distributed into the flue gas. A 2.63 μg/(N m<sup>3</sup>) amount of Hg was predicted at the inlet of ESP, where 1.72 μg/(N m<sup>3</sup>) is removed. At the inlet of the wet FGD system, 0.92 μg/(N m<sup>3</sup>) of Hg can be expected to be present, where 0.03 μg/(N m<sup>3</sup>) is removed along with sludge and effluents. About 0.62 μg/(N m<sup>3</sup>) of Hg in the flue gas emission from the stack can be expected.

The Hg mass distribution scenarios presented above demonstrated that emission and distribution of Hg during coal combustion can be estimated by having the elemental compositions and Hg contents in any coal. Further, Hg emission and speciations variations, depending on the coal elemental compositions, coal Hg and coal Cl contents, and boiler-operating conditions (temperature and air/fuel ratio, etc.), can also be predicted. Hence, this approach might be useful for predicting and understanding Hg mass distribution without measuring in the real plant. Of course, more consistent real measurement data including other parameters such as gas composition, HCl, SO<sub>x</sub>, and NO<sub>x</sub>, and unburned carbon content in the fly ash will give a more reliable prediction. To obtain more reliable distribution of Hg in coal-fired power plants and its fate in the environment, long-term studies are suggested.

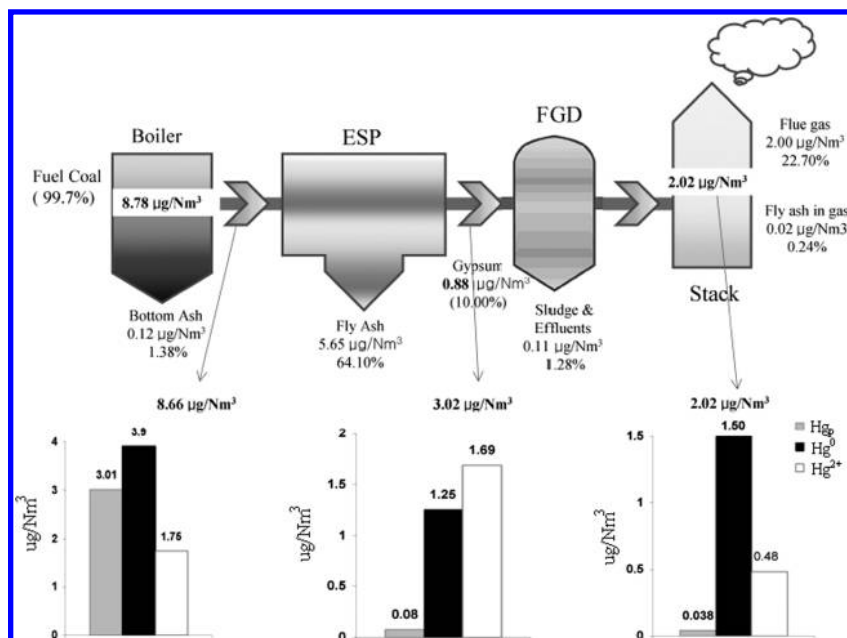


Figure 4. Distribution of mercury in coal power plants using NCA coal.

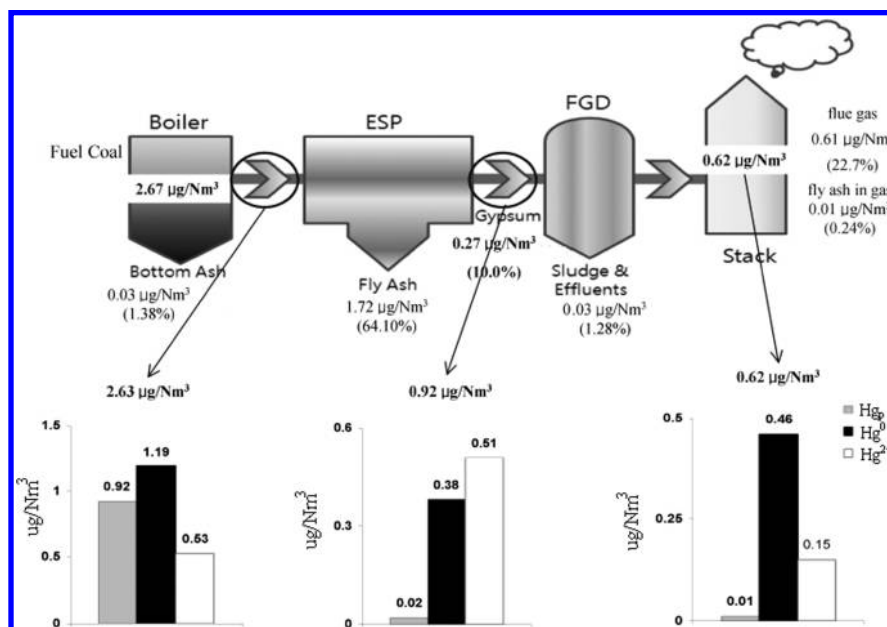


Figure 5. Distribution of mercury in coal power plants using blended coal (NCA:Ensham coal mixing ratio of 0.13:0.87).

#### 4. Summary and Conclusion

The mass distribution of Hg in power plants with a computer simulation program in combination with the measurement results at the real plant was presented. Hg concentration in bituminous coals used in Korean power plants ranged from 0.012 to 0.068 mg/kg with an average value of 0.046 mg/kg. The average Hg emission concentration at the boiler outlet and the stack of the tested power plant were 2.67 and  $1.59 \mu\text{g}/(\text{Nm}^3)$ , respectively. Hg transformation and oxidation in coal combustion flue gas was nonlinear and complex. At the boiler outlet, Hg was mainly speciated into  $\text{Hg}^0$  followed by  $\text{Hg}_p$  and  $\text{Hg}^{2+}$ . Upon decreasing temperature and interaction with the flue gas components the share of  $\text{Hg}^{2+}$  increased when passing through the ESP. A major portion of  $\text{Hg}^{2+}$  was removed in wet FGD. Finally,  $\text{Hg}^0$  was dominant in the stack emission. The measured data and the

equilibrium calculation showed that coal composition and APCDs configuration mainly affected the Hg concentration and speciation at the stack emission.

In a bituminous coal power plant, 57.6–64.3% of Hg entering into the system was captured in the ESP fly ash, 4.5 to 12.9% of Hg was removed in the FGD gypsum and 0.5–1.9% in FGD effluents, and 0.8–1.8% of Hg was removed in the boiler bottom ash. Finally, the remaining 15.2–27.0% Hg was released into the atmosphere.

The approach we presented here could be useful for obtaining the emission and distribution of Hg in any plant with coal information and process configuration. More reliable numbers of real measurements including other flue gas components and the carbon content in the fly ash will give better prediction.



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