Original Paper

Mercury Partitioning in Coal-fired Power Plants in Japan

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To evaluate mercury partitioning in a coal-fired power plant and to investigate the influence of the configuration of gas treatment facilities on mercury emission, data sets of mercury concentration in coal, coal combustion residues, wastewater, and stack gases were collected from 44 coal-fired power plants in Japan from 2001 to 2014. The mean mercury concentration in coal, measured from 1224 samples, was 0.039 mg/kg, while the mean emission rate, measured from 259 samples, was 3.63 $\mu\text{g}/\text{kWh}$. The total annual mercury emission from coal-fired power plants in Japan, which was calculated using the mean emission rate, was 1.0 t. The mercury removal efficiency was found to be improved by decreasing the electrostatic precipitator (ESP) operation temperature and by implementing selective catalytic reduction (SCR). The combination of SCR, advanced low-temperature ESP, and flue gas desulfurization (FGD) showed a high mercury removal efficiency of 87.4% on average.

日本の石炭火力発電所にて、2001年から2014年に測定された石炭、石炭灰、排水、および排ガスに含まれる水銀濃度の結果を収集し、石炭火力発電所における水銀の分配、および水銀排出に及ぼす排煙処理装置構成の影響を調査した。日本の石炭火力発電所で使用された石炭1224データの平均は0.039 mg/kgであり、発電電力量あたりの大気への水銀排出量(排出原単位)の平均は3.63 $\mu\text{g}/\text{kWh}$ であった。この排出原単位と2014年の発電電力量から求められる大気への年間排出量は1.0トンと推算された。石炭火力発電所における水銀除去率は、脱硝装置が設置され、電気集じん装置の操作温度が低いほど高くなる傾向であり、脱硝装置、低低温電気集じん装置、および湿式脱硫装置を設置した発電所の水銀除去率は、平均で87.4%と最も高い値であった。

Key Words

Mercury, Emission, Removal efficiency, Coal-fired power plant, Flue gas treatment facilities

1. Introduction

Coal combustion is globally recognized as a major emission source of mercury¹⁾. In the Minamata Convention on Mercury which entered into force on August 2017, coal-fired power plants and coal-fired industrial boilers were listed as the target sources of mercury emission regulation. In Japan, to ratify the Convention, the amendment of the Air Pollution Control Act that regulates mercury emission to the atmosphere was promulgated in June 2015 and executed in April 2018. In the amendment of the Air Pollution Control Act, the obligation of such facilities to comply with the emission limits value is stipulated. The emission limits value was set 10 $\mu\text{g}/\text{m}^3$ for the existing coal-fired power plants and 8 $\mu\text{g}/\text{m}^3$ for the newly constructed

power plants²⁾.

High-performance air pollution control facilities for NO_x, SO_x, and particulate matter (PM) have already been installed at most of the coal-fired power plants in Japan, as shown in Fig. 1. Although these facilities were not primarily installed for mercury removal, they have co-beneficial effects on the removal of environmental pollutants, including mercury. Gaseous oxidized mercury is removed by a wet flue gas desulfurization (FGD) facility, while particulate mercury is removed by a PM collector, such as an electrostatic precipitator (ESP) or a bag filter (BF)^{3)~5)}. Even though the SCR facility does not remove mercury, the catalyst causes changes in mercury speciation by promoting the oxidation of gaseous elemental mercury into a gaseous oxidized form and improves the mercury removal efficiency of wet FGD.

In 2006, mercury emission from coal-fired power plants in Japan was reported on the basis of mercury

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Fig. 1 Ratio of various configurations of flue gas treatment facilities of coal-fired power plants based on plant capacity in Japan in 2014

emission data collected before 2000⁶⁾. However, the influence of the configuration of gas treatment facilities on mercury emissions was not discussed. This report updates the statistics on mercury emission from coal-fired power plants in Japan by using data collected from 11 Japanese electric power companies from 2001 to 2014, and evaluates mercury partitioning in a coal-fired power plant.

2. Mercury concentration in coal

Mercury concentration in coal is an important parameter affecting the amount of mercury emissions. Data on mercury concentration in various coals, mainly bituminous coals, were collected from 17 power stations of Japanese electric power companies. The frequency distribution of mercury concentration in coal is shown in Fig. 2. The mercury concentration in coal appears to approximately follow a lognormal distribution. In the case of a lognormal distribution, the geometric mean is generally selected as the representative quantity. However, the geometric mean is lower than the arithmetic mean and may result in underestimation of the total concentration. Therefore, in this research, the arithmetic mean of the data was used as the representative value. The total number of samples for evaluating mercury concentration in coal was 1224, and the arithmetic mean, maximum, and minimum values of mercury concentration in coal were 0.039 mg/kg, 0.62 mg/kg, and 0.001 mg/kg, respectively. The mean value of mercury concentration in coal from 2001 to 2014 was slightly lower than that before 2000 (Mean mercury concentration of 181 samples: 0.045 mg/kg)⁶⁾. The total mercury annually fed into boilers was estimated to be 3.1 t, based on the coal consumption of 8.0×10^7 t in the power

Fig. 2 Frequency distribution of mercury concentrations in coal used at coal-fired power plants in Japan

stations of 11 electric power companies in 2014.

3. Mercury partitioning in a coal-fired power plant

Mercury is nearly volatilized from coal during combustion in a coal-fired power plant, and it is converted into clinker ash, fly ash, wastewater, sludge, gypsum, and stack gas. To update mercury emission data reported in 2006⁶⁾ and to investigate mercury partitioning in a coal-fired power plant, data on mercury concentration in coal combustion residues (clinker ash, fly ash, gypsum, and sludge), wastewater, and stack gas were collected from 27 power stations of Japanese electric power companies. In this research, the data below the determination limit were set at half of the determination limit value.

3.1 Mercury concentrations in coal combustion residues and wastewater

The mercury concentrations in coal combustion residues and the frequency distribution of the mercury concentrations are shown in Table 1 and Fig. 3 (a), (b) and (c).

Coal ash was mainly discharged from the boiler bottom and PM collector. To evaluate the mercury concentration in clinker ash discharged from the boiler

bottom, 87 samples were collected from 18 power plants. Most of the mercury concentrations in clinker ash were below the determination limit value. The detected concentrations were slightly higher than the detection limit values, and were negligible.

The arithmetic mean of mercury concentrations in fly ash collected by the PM collector was 0.15 mg/kg. Mercury concentrations in 137 samples of fly ash collected

Table 1 Mercury concentration in coal combustion residues

		Mean	Minimum	Maximum	Number of samples	Number of stations (power plants)
Fly ash	mg/kg	0.15	0.00025	1.0	739	25 (40)
Gypsum	mg/kg	0.43	0.00025	2.8	176	16
Sludge	mg/kg	6.7	0.02	71	278	17

(a) Fly ash

(b) Gypsum

(c) Sludge

Fig. 3 Frequency distribution of mercury concentrations in coal combustion residues

by high-temperature ESPs (H-ESPs) operated at around 623 K were below the determination limit value. On the other hand, the mean value of mercury concentration in fly ash collected by low-temperature ESPs (L-ESPs) operated at 403–423 K was 0.16 mg/kg (366 samples), while that in fly ash collected by advanced low-temperature ESPs (LL-ESPs) operated at 363–373 K was 0.23 mg/kg (232 samples). The mercury concentrations in fly ash collected by LL-ESPs were generally higher than those collected by L-ESPs because the mercury adsorption on fly ash increases at lower temperatures⁷⁾.

The wet limestone-gypsum process for SO_x removal is adopted at most of the coal-fired power plants in Japan. The arithmetic means of mercury concentrations in gypsum and sludge in effluent treatment facilities were 0.43 mg/kg and 6.7 mg/kg, respectively. All the data (681 samples) in wastewater showed lower mercury concentration in wastewater than the effluent standard (0.005 mg-Hg/L) of Japan. Mercury removed by wet FGD is generally transferred to gypsum and sludge.

3.2 Mercury emissions

To investigate the mercury emissions from coal-fired power plants in Japan, data on mercury concentration in stack gases were collected from 43 power plants. The effect of the plant configurations on mercury emissions was also investigated.

3.2.1 Mercury concentrations in stack gases

Mercury exists in gaseous and particulate forms in stack gases. To evaluate the mercury concentrations in stack gases, 270 samples of gaseous mercury were collected

from 33 power plants and 281 samples of particulate mercury were collected from 34 power plants. The impinger method with an aqueous acidic solution of potassium permanganate was used to sample gaseous mercury from stack gases. Fly ash in the stack gases was isokinetically collected on a filter, and it was digested for analysis via cold vapor atomic absorption spectroscopy (CVAAS).

The frequency distributions of gaseous and particulate mercury concentrations in stack gases are shown in Fig. 4 (a) and (b). The mean value of gaseous mercury concentrations was 1.3 $\mu\text{g}/\text{m}^3$, and the maximum value was 13 $\mu\text{g}/\text{m}^3$. Further, the mean value of particulate mercury concentration in stack gases was 0.0072 $\mu\text{g}/\text{m}^3$. The frequency distribution of the ratio of particulate mercury to the total mercury in stack gases is shown in Fig. 5. This ratio was lower than 5% in more than 90% of the samples, and it trends to increase as the total mercury concentration in the stack gases decreased as shown in Fig. 6. The mercury emission rate, i.e., the quantity of mercury emitted while producing unit electric power, was calculated using the gas emission volumes and the generated electricity. In this calculation, 259 samples collected from 28 power plants were used. The mean value of the mercury emission rate was estimated to be 3.63 $\mu\text{g}/\text{kWh}$.

3.2.2 Influence of configurations of gas treatment facilities

The configuration of gas treatment facilities is possibly the major factor affecting the emission characteristics as well as the coal properties, such as the concentrations of mercury and chlorine in coal.

The mercury removal efficiency is the ratio of the

Fig. 4 Frequency distribution of mercury concentrations in stack gases

Fig. 5 Frequency distribution of the ratio of particulate mercury to the total mercury in stack gases

Fig. 6 Relation between the total mercury concentration and the ratio of particulate mercury to the total mercury in stack gases

Fig. 7 Mercury removal efficiency by gas treatment facilities

quantity of mercury removed in a plant to the quantity of mercury fed to the boiler. In this calculation, 195 samples collected from 24 power plants were used. The mean values of the mercury removal efficiencies classified by the configurations of gas treatment facilities are shown in Fig. 7 with the 25th and 75th percentiles. The highest mean mercury removal efficiency of 87.4% was observed for the configuration of SCR, LL-ESP, and FGD. Although only two samples were available for BF, the mercury removal efficiency of a plant with BF installed was found to be nearly the same as that of a plant that implemented SCR, L-ESP, and FGD. Furthermore, the mercury removal efficiency was found to increase as the ESP temperature decreased.

This is because the amount of mercury captured in the fly ash is proportional to the amount of unburned carbon in the fly ash, and it increases at lower temperatures⁷⁾. In addition, the removal efficiency was found to increase when SCR was implemented, because SCR promotes the oxidation of gaseous elemental mercury and mercury removal in FGD.

3.3 Partition of mercury in a coal-fired power plant

To investigate the partitioning of mercury in a coal-fired power plant, the amount of mercury annually discharged into coal combustion residues and emitted into stack gases was estimated using the mean values of the

Table 2 Annual amount and transfer ratio of mercury in coal-fired power plants in Japan

	Annual amount [t/y]	Transfer ratio [%]	Base of calculation
Fly ash	1.2	38.7	total amount of fly ash discharged from PM collector: 7.7×10^6 ton
Gypsum	0.69	22.3	total amount of gypsum: 1.6×10^6 ton
Sludge	0.44	14.2	total amount of sludge : 6.5×10^4 ton
Stack gas	1.0	32.9	total electricity from coal-fired power plants: 2.82×10^{11} kWh

mercury concentration in the coal combustion residues (see Table 1). The emission rate was $3.63 \mu\text{g/kWh}$. The results are summarized in Table 2. The sum of the proportions was 108.1% and the transfer ratio to the PM collector, FGD, and stack were estimated to be 38.7%, 36.5%, and 32.9%, respectively. In this calculation, the total annual emission quantity was 1.0 t. The amount of mercury emissions from stationary sources to air in Japan in 2014 was estimated as $17 \text{ t/y}^{1)}$, and the contribution of the coal-fired power plants of 11 utility companies was approximately 5.9%.

4. Conclusions

To evaluate mercury emission from coal-fired power plants into the atmospheric environment in Japan and to investigate the influence of the configuration of gas treatment facilities on mercury emissions, data on mercury concentrations in coals, coal combustion residues, wastewater, and stack gases were collected from coal-fired power plants of 11 electric power companies. The mercury emission rate was estimated to be $3.63 \mu\text{g/kWh}$, and the annual emission quantity of mercury was estimated to be 1.0 t. Furthermore, the mercury removal efficiency was

found to be improved by decreasing the ESP temperature and installing the SCR facility. The combination of SCR, advanced low-temperature ESP (LL-ESP), and wet FGD can achieve a high mercury removal efficiency of 87.4% on average.

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