

Mercury emissions from polish pulverized coal-fired boiler

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Abstract. The current paper presents the research results carried out at one of Polish power plants at a pulverized hard coal-fired 225 MW unit. The research was carried out at full load of the boiler (100% MCR) and focused on analysis of mercury content in the input fuel and limestone sorbent for wet flue gas desulfurization (FGD) system, as well as investigation of mercury content in the combustion products, i.e. fly ash, slag, FGD product (gypsum) and FGD effluents (waste). Within the framework of the present study the concentration of mercury vapor in the exhaust gas was also investigated. The analysis was performed using Lumex RA-915+ spectrometer with an attachment (RP-91C). The measurements were carried out at three locations, i.e. before the electrostatic precipitator (ESP), downstream the ESP, and downstream the wet FGD plant. Design of the measurement system allowed to determine both forms of mercury in the flue gas (Hg^0 and Hg^{2+}) at all measurement locations. Based on the measurement results the balance of mercury for a pulverized coal (PC) boiler was calculated and the amount of mercury was assessed both in the input solids (fuel and sorbent), as well as the gaseous and solids products (flue gas, slag, ash, gypsum and FGD waste).

1 Introduction

Getting rid of pollutants, such as sulfur dioxide, nitrogen oxides or particulate matter, that are emitted to the atmosphere due to the combustion processes associated with the production of electricity and/or heat has become an important issue. The next step in the aim to protect the environment will be focused on the reduction of heavy metal emission, particularly mercury, cadmium, or lead [1].

One of the main instruments supporting the reduction of mercury emission is Minamata Convention that had been drawn up in Kumamoto, Japan, in October 2013 and signed by the Polish Government in September 2014. The Convention has become an international act with a global reach; its main aim is to protect both human health and the environment from negative affections brought about by anthropogenic emissions of mercury and its compounds. Until the end of 2016 the Minamata Convention had been ratified by 35 countries [2].

Mercury is usually determined in Earth's crust at the level of roughly 0.05 ppm. The most important mercury-containing minerals are: cinnabar (HgS), calomel (Hg_2Cl_2), and native

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mercury, all highly toxic, as well as the dimethylmercury that is formed in aquatic environment by microorganisms. The dimethylmercury is particularly dangerous since it is absorbed by and accumulated in living organisms [3].

New BAT (Best Available Technology) rules, which will soon be implemented for mercury emission associated with the combustion of solid fuels in power plants, very strictly point out the need to control and minimize the emission of mercury particularly that the emission from a single Polish power plant boiler may even yield roughly 50 kg/year [5]. The Hg-problem might become even more difficult for China where in 2010 the anthropogenic emission of mercury was estimated at roughly 576 Mg (i.e. over 35% of total global emission) [6].

It is estimated that the total emission of mercury yield somewhere between 5 and 15 thousand ton per year, and roughly 30-50% of that emission is of associated with human activity. From the anthropogenic emission more than half of mercury compounds emitted to atmosphere is contributed by the combustion of fossil fuels since millions tons of hard coal and lignite are being burned every year to produce electricity and heat.

High temperature conditions in the furnaces favor series of chemical reactions leading to the decomposition of mercury-containing chemical compounds. Practical result of those reactions is the presence of only gaseous metallic mercury, Hg^0 , in the flue gas at temperatures above 900°C. Cooling of the flue gas and the presence of such components as NO_2 , HCl, SO_2 , H_2O , or Cl_2 , may then favor the oxidation of mercury and/or their adsorption by fly ash particles. As a result, mercury emitted from fossil fuel combustion plants may exist in three forms, i.e. either elemental mercury (volatile metallic mercury) gas, Hg^0 , oxidized gaseous mercury (volatile ionic mercury), Hg^{2+} , or mercury adsorbed on dust particles, $Hg_{(p)}$ [4, 7]. Due to very low mercury content in coals (usually 80-100 ng/g as in the case of Polish coals [16, 17, 18]) and its random distribution in fuel particles the exact measurement of mercury becomes quite difficult. Most common mercury analyzers are operated based on atomic adsorption spectrometry with atomic vapor generation (CV-AAS). In that method the sample is burned and mercury vapors are accumulated on a gold sorbent trap; later on then deposit is heated and mercury vapors are determined. Another way to detect mercury is the Zeeman spectroscopy method with high frequency modulated polarization of light; the method enables to determine mercury content without accumulation on the gold sorbent. The sample is introduced into a heated chamber where it is burned and the mercury vapor concentration is determined on-line. Some other convenient way is the use of mercury traps. Despite various measurement techniques applied, the results and the determination of mercury content in solid samples are comparable and in a good agreement, as confirmed e.g. in [18].

So far, the investigation of mercury emissions from fossil fuel burning power plants has been the subject of several publications. Tang and Pan [8] reported emission of mercury from two 600 MW pulverized coal fired boiler systems. One of the system was equipped with wet flue gas desulphurization (FGD) facility and electrostatic precipitator (ESP). The mercury was introduced to the system with coal and limestone and the overall mercury load was estimated as 13.62 g/h. The largest amount of mercury, 3.73 g/h, was captured by wet FGD plant; accumulation on fly ash particles was just 0.7 g/h, while the mercury in the flue gas was calculated as roughly 5.27 g/h. The other boiler system investigated by Tang and Pan [8] was additionally equipped with an SCR (selective catalytic reduction plant) to control the emission of NO_x . The main source of Hg was again coal and sorbent and mercury input to that boiler system was estimated as 7 g/h. The amount of mercury emitted to atmosphere was roughly 0.17 g/h; the majority of Hg was captured by fly ash particles (3.77 g/h) and gypsum (2 g/h).

Pudasainee et al. [9] also investigated the emission of mercury from a number of South Korean supercritical 500-600 MW pulverized hard coal fired power plants. The power generating facilities were equipped with SCRs, ESPs and wet FGDs. The authors reported

that the total amount of mercury was introduced with coal and its concentration in the flue gas in the furnace was about 27.3 mg/Nm^3 and that the amount of Hg^{2+} in the flue gas downstream the SCR facility increased significantly from 3.7% to 14.7%. The measurements carried out downstream the ESP indicated that the amount of mercury in the flue gas decreased to roughly 8.5 mg/Nm^3 and over 82% of the mercury was in the form of Hg^{2+} . The measurements at the stack indicated that downstream the FGD plant the emission of mercury decreased to 2.9 mg/Nm^3 , and the share of Hg^{2+} was roughly 46%. As reported by the authors, the share of various forms of mercury determined for other power generation facilities were quite similar.

Burmistrz et al. [10] investigated the emission of mercury from two (370 MW and 225 MW) Polish power plants burning hard coal. One of the facilities was equipped with an SNCR (selective non-catalytic reduction system to control the emission of NO_x), as well as the ESP and wet FGD. As reported, over 10.5 g/h of mercury was introduced to the boiler system. Downstream the ESP the mercury content in the exhaust gas was reduced to roughly 4 g/h, and downstream the wet FGD it was decreased to 2.5 g/h. The reduction was mainly caused by fly ash particles which carried more than 7.7 g/h of mercury. The gypsum (product of wet FGD plant) carried out slightly more than 1.8 g/h of Hg. In case of the other facility the mercury input was estimated at roughly 7.9 g/h. Lack of the SNCR brought about that the amount of mercury captured by the ESP was lower, just roughly 4.8 g/h. The operation of wet FGD was reported quite poor since only 0.53 g/h of mercury was captured there and over 3.6 g/h was emitted to the atmosphere via the stack.

As briefly discussed above, the data and results reported by various authors may differ quite significantly. Consequently, detailed industrial data are still needed in order to assess properly current emissions of mercury. Therefore, the intention of this paper is to provide some data on emission and balance of mercury in a 225 MW pulverized hard coal fired power generation plant in Poland.

2 Research methodology

The tests were carried out at a 225 MW plant burning Polish hard coal. The boiler system was equipped with SNCR, ESP, and wet FGD. The investigations were carried out at two locations, i.e. downstream the ESP and downstream the wet FGD. Unfortunately, due to technical reasons it was not possible to carry out measurements upstream the ESP. The investigations were focused on flue gas sampling from those two locations and the determination of mercury, Hg^0 , and Hg^{2+} . Furthermore, the amount of mercury in coal, sorbent, fly ash, slag, and gypsum (wet FGD product) was also determined. Sampling locations are schematically shown in Fig. 1.

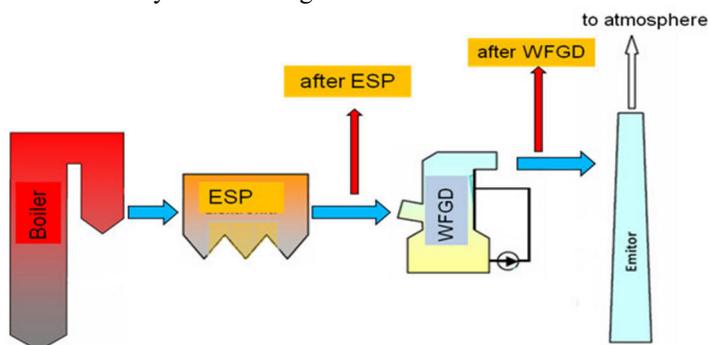


Fig. 1. Locations of mercury samplings.

The determination of mercury was carried out with the use of a mercury analyzer RA-915+ produced by Lumex corporation. The analyzer is a spectrometer operated based on the Zeeman effect (Zeeman Atomic Absorption Spectrometry with High Frequency Modulated Light Polarization, ZAAS-HFM) and allows to avoid the need for accumulation of mercury on a gold sorbent trap. The concentration of mercury in the gas phase can be determined directly by sucking in the gas to the measurement section of the spectrometer via an internal pumping device.

In order to determine mercury concentrations in solid samples the spectrometer 'Lumex' was coupled to an additional RP-91C device. The measurements could be carried out for mercury concentrations between 0.5 mg/kg and 10,000 mg/kg; the maximum error was $\pm 20\%$. The speciation of mercury was possible due to the determination of Hg^0 mercury directly by Lumex spectrometer, and the application of a part of commonly known Ontario Hydro method that allowed the investigation of Hg^{2+} mercury. The sampling device that was inserted into the measurement zone consisted of two equally long tubes connected to each other. The tubes were heated with by a ribbon heater that allowed to maintain the temperature high enough to prevent any condensation of steam. The temperature of the heating band was maintained by a temperature controller. The flue gas was parallelly sampled: via one of the tubes directly to Lumex spectrometer, while the other tube transported the flue gas to the atmosphere via a glass impinger trap. Each of the impingers in the trap contained 100 ml of KCl, allowing the dissolution of mercury Hg^{2+} . The impingers were placed in specially-designed containers where constant temperature of roughly 10°C was maintained. No filters were placed upstream the impingers and the spectrometer. The determination of Hg^{2+} mercury captured in the impingers was carried out in laboratory with the application of a cold vapor technique, where the mercury dissolved in KCl was snatched away with SnCl_2 (100 g/dm³) [15]. Both sampling tubes that were inserted into the measurement zone were made of stainless steel while all other connectors were manufactured of silicone. One single measurement consisted of two 30-minute sampling times separated by a 60 minute interval. In each case the results presented in this paper are the averages of two corresponding measurement runs. The schematics of the sampling system is shown in Fig. 2.

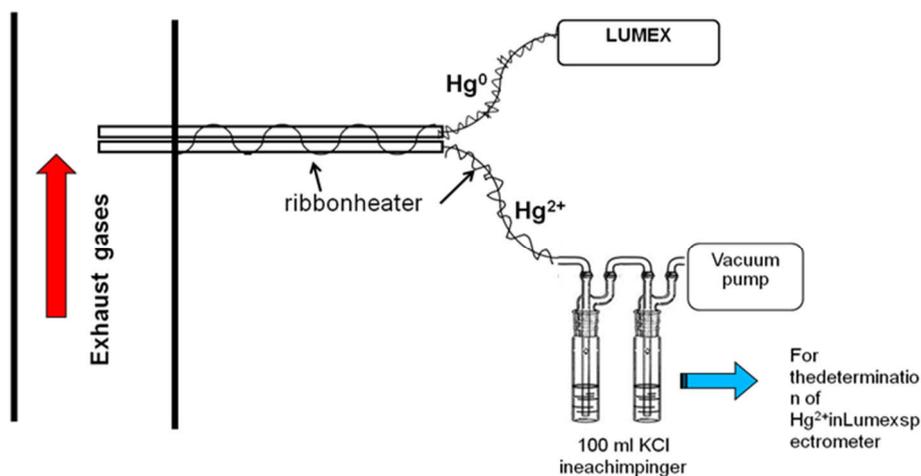


Fig. 2. Sketch of the sampling system to determine both mercury Hg^0 and Hg^{2+} .

3 Results and discussion

During the measurement campaign at the plant the boiler was fired with a blend of hard coals from Polish mines. Ultimate and proximate analysis of the coals is shown in Table 1.

Table 1. Main parameters of coal combusted at the plant during the tests (except for transient moisture, all other values are given as ‘air dry’)

Parameter	Unit	Value
Transient (external) moisture, as received	%	13.6
Internal (hygroscopic) moisture	%	6.9
Ash	%	27.8
Volatile matter	%	23.2
Fixed carbon	%	42.1
Higher heating value, HHV	kJ/kg	21600
Lower heating value, LHV	kJ/kg	20700
Carbon, C	%	55.2
Total mercury, Hg	ng/g	153.6

The content of mercury in substrates and combustion products are shown in Table 2 as determined at the plant. Based on the data on mercury concentrations in various substances (cf. Table 2), as well as the information on flue gas, ash, slag, coal, and sorbent flow rates in the boiler system the flows of mercury (mg/s) at various locations were calculated and also shown in Table 2. As can be seen, the balance of mercury is in a very good agreement since the difference between mercury input and output does not exceed 11%.

Table 2. The balance of Hg for a 225 MW pulverized hard coal fired boiler

		Hg content	Flow rates: solids [kg/s]; gas [Nm ³ /s]	Hg flow rate [μg/s]	Mass balance [%]
Inlet	Coal	135.6[ng/g]	22.43	2259.6	89.8
	Limestone	9.0[ng/g]	2.25	20.0	
Outlet	Fly ash	180.1[ng/g]	3.78	728.3	
	Slag	5.2[ng/g]	1.62	5.29	
	Gypsum	156.1[ng/g]	4.11	587.3	
	FGD waste	111.3[ng/g]	0.11	4.57	
	Hg ⁰ in flue gas	1450[ng/m ³]	187.5	272.7	
	Hg ²⁺ in flue gas	2400 [ng/l]	187.5	450.0	

Figure 3 shows the amount of mercury introduced with coal and sorbent to the boiler system and the mercury that is transported with combustion products (fly ash, slag, flue gas, gypsum, and FGD waste). As it may be seen, the mercury in the combustion products was mainly determined in the fly ash, gypsum and the flue gas. In case of the flue gas roughly 60% of mercury was in the form of Hg²⁺.

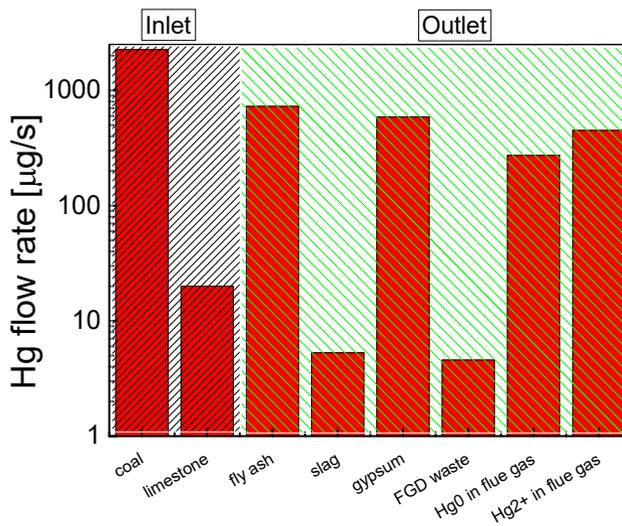


Fig. 3. Mercury mass balance for the pulverized coal fired 225 MW boiler.

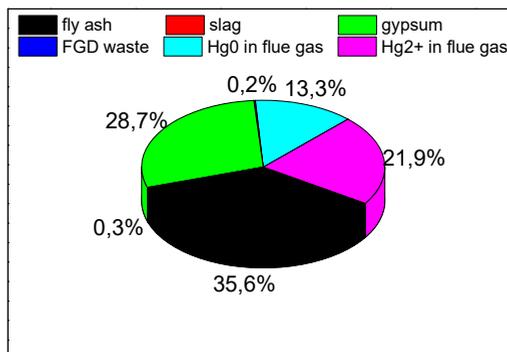
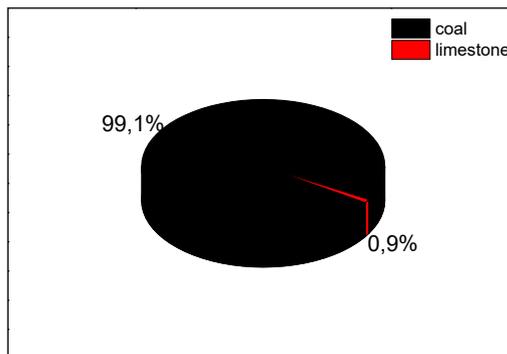


Fig 4. The shares of individual input and output components and their contribution to mercury inventory.

The shares of individual substrates and products, as well as the quantities of mercury and mercury inventory for the boiler system are shown in Fig. 4. Analysis of the results indicates that the major source of mercury (over 99%) is coal; the amount of mercury introduced with sorbent is negligible (less than 1%). As for mercury output, the largest shares, roughly 35% of total Hg, are contributed by both fly ash and flue gases. In the latter case, the majority of mercury is in the form of Hg^{2+} (22% of the total mercury input) – the contribution of Hg^0 is just 13.3% of the input mercury. The contribution of gypsum mercury is slightly lower and has been estimated as roughly 29% of total mercury input load. Since the oxidized form of mercury can be easily dissolved in water [12,13] it is commonly accepted that wet FGDs are usually very effective and can remove over 90% of Hg^{2+} mercury from the flue gas. However, in some cases, the efficiency of mercury removal in wet FGD plants may be, surprisingly, significantly lower, usually due to non-optimized operation or inappropriate chemical conditions in the scrubber [11].

4 Summary

The results presented and discussed in the current paper may be briefly summarized as follows:

- 1) For the boiler system investigated, the main source of mercury (over 99%) was coal containing almost 136 ng/g of Hg.
- 2) Roughly 36% of the total mercury was discharged with exhaust flue gases; however, comparable amounts were determined in the fly ash (35% of total Hg) and gypsum (29% of the input mercury).
- 3) The majority of flue gas mercury was determined as Hg^{2+} contributing to roughly 22% of the total mercury input. The share of Hg^0 was lower and estimated as roughly 13% of the total mercury input.

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