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Research article

Lignites and subbituminous coals combustion in Polish power plants as a source of anthropogenic mercury emission

Piotr Burmistrz [a,*], Krzysztof Kogut [a], Marta Marczak [a], Jerzy Zwoździak [b]

[a] AGH University of Science and Technology, Faculty of Energy & Fuels, 30 Mickiewicza Avenue, 30-059 Kraków, Poland
[b] Wrocław University of Technology, Faculty of Environmental Engineering, 27 Wybrzeże Wyspiańskiego St, 50-370 Wrocław, Poland

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ABSTRACT

Coal combustion is one of the main anthropogenic sources of mercury emission to the atmosphere. A total of 121 subbituminous coal samples and 29 lignite samples representative for coals burned in Polish power and heat and power plants were acquired and examined. The average mercury content in subbituminous coal samples was 104 μg kg^{-1} (4.591 g Hg TJ^{-1}), varying from 18 to 518 μg kg^{-1}. The average chlorine and bromine content were 2200 ppm and 12 ppm, respectively. For lignite samples the average mercury content was 197 μg kg^{-1} (21.380 g Hg TJ^{-1}), varying from 60 to 665 μg kg^{-1}. Lignite samples contained significantly less chlorine (40 ppm on average) and bromine (4 ppm) than coal samples. The $Cl \cdot Hg^{-1}$ ratio for subbituminous coal samples varied between 10^3 and 10^5. For lignite samples this ratio was around 10. Mercury mass balances were performed for two subbituminous coal-fired plants and one lignite-fired plant. The chemical composition of each type of coal had a significant influence on mercury concentration and speciation in the flue gas. The proportion of oxidized mercury (Hg^{2+}) correlated with chlorine content. The relatively large proportion of particulate-bound mercury (Hg_p) and Hg^{2+} measured favored mercury removal by the electrostatic precipitator (65% on average), and by the wet flue gas desulfurization units (32%). Results of mercury emissions from the stack to the atmosphere were 2.0–5.0 and 15.1 μg m^{-3}, for plants burning subbituminous coal and lignite, respectively. The mercury leaving the stack from three plants was over 90% elemental mercury (Hg^0). Calculated mercury emission factors for plants burning subbituminous coal and lignite were: 0.71–1.80 g Hg TJ^{-1} (subbituminous coal) and 6.09 g Hg TJ^{-1} (lignite).

1. Introduction

Mercury is a highly toxic, heavy metal for which human organism shows no physiological demand. Due to its toxicity, global distribution from emission source, and long atmospheric residence time [1], mercury and its compounds have been classified by the US Environmental Protection Agency (US EPA) as Hazardous Air Pollutants (HAPs) [2]. Worldwide studies commissioned by United Nations Environment Programme (UNEP) have confirmed harm from global mercury emissions, which have justified action to be undertaken at the international level [3].

The presence of mercury in the environment results from both natural and anthropogenic sources [4–6]. Natural mercury emission to the atmosphere is estimated at 5200 ± 2700 Mg yr^{-1} [4,5,7]. Anthropogenic emission between 2000 and 2005 was estimated to be between 1926 and 2320 Mg yr^{-1} [8–10]. Global anthropogenic mercury emission to air from different sectors in 2010 was estimated at approximately 2000 Mg [11]. The biggest shares in this emission were: artisanal and small-scale gold mining (37%), coal combustion (24%), mining, smelting and production of non-ferrous metals (10%) as well as cement production (9%). Average mercury emission in the EU in 2010 was 87.5 Mg, varying from 43.6 to 225.3 Mg. This emission resulted from combustion (over 50%), cement production (15%) and non-ferrous metals production (13%) [11].

Alongside Germany, Poland is a country with highest annual mercury emission in Europe. It is estimated to range from 10 Mg to nearly 20 Mg [11–13]. The main share of these emissions is due to coal combustion for generation of electric power and for heating. In 2013 about 87% [14] of electricity and heat in Poland were generated by combustion of 35,325,000 Mg of subbituminous coal and 61,769,000 Mg of lignite [15]. Emissions reported for Poland applying new emission factors for subbituminous coal (1.498 g Hg TJ^{-1}) and lignite (6.906 kg Hg TJ^{-1}), were 10,115.8 kg of mercury in 2010, 10,020.1 kg in 2011, 10,357.8 kg in 2012 and 10,376.0 in 2013. Approximately 56% was due to coal combustion of coal for production of electricity: 5640.4 kg, 5615.0 kg, 5776.6 kg and 5760.8 kg in 2010, 2011, 2012 and 2013, respectively [12,13].

* Corresponding author.
E-mail address: burmistr@agh.edu.pl (P. Burmistrz).

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Average mercury content in subbituminous coals varies from 25 to 300 μg kg^{-1}, and in Polish lignites from 100 to 450 μg kg^{-1} [16–20]. By comparison, average mercury content in bituminous coals and lignites burned in US power plants is: 171 μg kg^{-1} for lignites, 69 μg kg^{-1} for subbituminous coals and 81 μg kg^{-1} for bituminous coals [21].

In China where anthropogenic mercury emissions are estimated to be the highest in the world, coals have an average mercury content of 144 μg kg^{-1}. Content varies for specific power plants from 10 to 385 μg kg^{-1} [22,23]. Estimated annual mercury emission from coal combustion in China varies from 161.6 to 219.5 Mg [24–26].

Research and full-scale test data confirm that mercury emission to the atmosphere depend on several factors [27–29]. These include: mercury content and chemical composition of burned coal, type of reactor, mercury speciation of flue gases leaving the reactor, types and efficiency of exhaust gas purification processes and presence of specified components in fly ashes and flue gases. During combustion, mercury in coal is transformed into three species: (i) particle-bound mercury (Hg_p); (ii) vapor-phase elemental mercury (Hg^0) and (iii) vapor-phase oxidized mercury (Hg^{2+}) [30]. Oxidized mercury is soluble in water and can be removed in wet scrubbers, e.g. in wet flue gas desulfurization units (WFGD). Hg_p is removed by dust control equipment such as baghouse filters and electrostatic precipitators (ESP). Elemental mercury (Hg^0) usually escapes emission control equipment and is emitted to the atmosphere [30,31]. Results from 84 power plants indicate that in total mercury emitted to the atmosphere, 87% is Hg^0, 5% Hg^{2+} and 8% Hg_p [32]. Therefore, the conversion of mercury from one form to another is important for selecting the appropriate mercury removal technology.

In Polish power plants and heat & power plants, subbituminous coal is burned in: (i) grates fitted with cyclones (CYC) or with electrostatic precipitators (ESP) (4% of the burned subbituminous coal); (ii) in pulverized coal boilers (PC), from which particles in flue gas are removed in ESP or by fabric filters (FF) (47%); (iii) in pulverized coal boilers fitted with ESP or FF and wet or dry flue gas desulfurization installations (WFGD or DFGD) (46%) and (iv) in fluidized bed boilers (FBC) with flue gas dust removal in ESP (3%). On the other hand, lignites are burned in PC fitted with: (i) ESP + WFGD (41%); (ii) ESP + DFGD (7%); (iii) ESP only (40%) and (iv) FBC with flue gas dust removal in ESP (12%) [18]. In recent years APCD in Poland are being fitted with Selective Catalytic Reduction (SCR) installations and Selective Non-Catalytic Reduction (SNCR) installations for the removal of nitrogen oxides and flue gas desulfurization installations – mainly wet, less frequently dry or semi-dry.

In this work, results of studies on mercury content in 121 subbituminous coal samples from 30 different Polish coal mines and 29 lignite samples from 5 deposits were examined. In addition to routine proximate analysis, sulfur, chlorine and bromine were also measured. Results for mercury distribution and speciation for three power plants are also presented. Two of these plants are subbituminous coal-fired and one is lignite-fired.

2. Experimental

2.1. Subbituminous coal and lignites sampling

Subbituminous coal (SBC) samples were acquired from supplies of 12 power plants and 3 heat and power plants in Poland (121 samples from 30 different coal mines were taken in total). Lignite (L) samples were obtained from 3 power plants, for which coal was supplied from 5 mines (29 samples in total). Automated samplers acquired samples from conveyor belts in motion in accordance with the ISO standard [33]. Each sample represented a batch of SBC of total mass ranging from 1400 to 4200 Mg, and a batch of L of total mass of at least 5000 Mg. Sealed samples were taken to the laboratory for analysis. The scope of analysis is described in Section 2.2. A sample acquisition diagram is shown in Fig. 1.

2.2. Analysis of coal samples

Air-dried samples were prepared in accordance with the ISO standard [34]. The scope of analysis included: proximate and ultimate analysis in accordance with the ISO standard [35,36], combustion in AC-350 bomb calorimeter (LECO) with Eschka mixture, potentiometric titration method of chlorine content, bromine content with X-ray spectrometry with wavelength dispersion in PROMUS II sequential spectrometer (Rigaku) using a bespoke research procedure and mercury content with absorptive atomic spectrometry with cold vapor (CV-AAS) generation in MA-2 automated mercury analyzer (Nippon Instruments Corporation). Values of these parameters were determined for the analytical state (air-dried) of the sample and then recalculated to dry and as-received states of samples in accordance with recalculation equations from the ISO standard [37].

2.3. Statistical assessment of results

The following statistics were calculated for each parameter of the investigated coal: arithmetic mean, standard deviation (SD), variability coefficient (CV), expanded uncertainty at 95% confidence level.

The measure of credibility for a single analytical sample examination is the uncertainty of the result considered as uncertainty including: sampling, preparation of general sample, preparation of analytic and laboratory samples and the analysis itself. The detailed procedure was described in previous work [38].

2.4. Power stations and sampling procedures

The configurations of the three Polish power plants tested in this study are provided in Table 1. A schematic diagram of the sampling campaigns in the sampled power plants is shown in Fig. 2.

The Ontario Hydro Method (OHM) [39] was used to determine Hg^0, Hg^{2+}, and Hg_p in flue gas samples. Representative samples were taken from the flue gas stream isokinetically through a glass-lined probe and a glass fiber filter at 120 °C, followed by a series of impingers immersed in an ice bath. Particle-bound mercury (Hg_p) was collected in the front tip of the sampling probe. The first three impingers containing 1 N potassium chloride solution were connected to absorb oxidized mercury (Hg^{2+}). The fourth impinger containing acidified hydrogen peroxide was used to absorb elemental mercury, and elemental mercury was mainly captured in the fifth, sixth and seventh impingers which contained the solutions of acidified potassium permanganate. In addition, an eighth impinger containing silica gel was provided to ensure that the flue gas was thoroughly dried before it left the impinger train. The concentration of mercury in the gas was measured at three different sampling points, (IN)-ESP, (OUT)-ESP and (OUT)-WFGD (see Fig. 2).

Tests for each power plant consisted of three periods of minimum 6 h each. During tests, representative samples for selected components were acquired. These included: coal supplying boiler, bottom ash, fly ash from ESP, limestone suspension and gypsum (see Fig. 2). The scope of analysis for SBC and L samples is described in Section 2.2.

2.5. Reliability assessment

Reliability of each measurement result was assessed with 95% uncertainty. The balance results for three power plants are arithmetic means from three measurement series. The reliability of these results was assessed with estimation error ($B_{1/2}$) calculated as follows:

$$B_{1/2} = \pm t_{\alpha/2;k=n-1} \cdot SD \cdot n^{-1/2} \quad (1)$$

where: SD – standard deviation, $t_{\alpha/2;\,k\,=\,n\,-\,1}$ – Student's t-test for $k = n - 1$ degrees of freedom and 95% confidence level, n – number of repetitions.