

ARCHIVES OF ENVIRONMENTAL PROTECTION

vol. 39

no. 2

pp. 141 - 150

2013



PL ISSN 2083-4772

DOI: 10.2478/aep-2013-0019

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THE INVESTIGATION OF MERCURY CONTENTS
IN POLISH COAL SAMPLES

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Keywords: Mercury, mercury removal, coal, enrichment of coals.

Abstract: This paper presents the results of the investigation associated with the determination of mercury content in Polish hard coal and lignite samples. Those coals are major fuels used for electricity generation in Poland. The results indicated that the average content of mercury in the coal samples was roughly about 100 ng/g. Apart from the determination of the mercury contents a detailed ultimate and proximate analysis of the coal samples was also carried out. The relationships between the mercury content and ash, as well as fixed carbon, volatile matter, sulfur, and high heating value of the coal samples were also established. Furthermore, the effect of coal enrichment was also investigated, and it was found that the enrichment process enabled the removal of up to 75% of the coal mercury from the samples.

INTRODUCTION

The combustion of hard coal and lignite is conducted mainly for power generation purposes. It is, however, associated with significant emission of pollutants and/or other unwanted combustion byproducts, such as, e.g., ash or slag. In order to decrease the emission and take care about the environment several 'combustion-associated' emission standards have been introduced in developed countries (e.g. for sulfur dioxide, nitrogen oxides, or particulate matter). Currently, there are many efforts made to decrease the emission of carbon dioxide [23]. The next possible actions will probably focus on decreasing the emission of mercury, lead and/or cadmium [22].

Mercury is a highly volatile element. Some forms of mercury may remain in the atmosphere for up to 2 years and during that time they may be transmitted over long distances, far away from the emitter. Over 95% of the world global mercury emission is the result of solid fuel combustion. Although the specific mercury content in coal is relatively small, roughly less than 100 ng/g, the annual emission from a coal fired boiler may reach almost 58 kg Hg [5]. Since the global world emission of mercury from coal combustion is recently estimated as 1474 t/y [18] the problem is quite serious and thus

there is a need to implement some regulations and decrease the emission of mercury from coal combustion facilities.

The United States was the first country where mercury emission from solid fuel combustion plants regulations were introduced. The similar works on the implementation of the emission standards in the European Union and Japan are currently going on and the situation is expected to change soon [21].

Three forms of mercury may generally exist in the environment, i.e. gaseous mercury, Hg^0 , inorganic mercury in the form of Hg^{2+}_2 or Hg^{2+} , and organic mercury that is associated with organic compounds (e.g. CH_3Hg^+ , CH_3HgCH_3 , etc.). The mercury in coal has been usually determined as clay-associated mercury, or mercury associated with organic matter (Hg_{org}), or sulphides (Hg_{sulf}) [16, 17]. The studies conducted by Zheng et al. [17] indicated that mercury was mainly found in the form of sulphides (39.5% of the total mercury in the samples) and organic compounds (29.9% of the total mercury) [17]. The results of the works published in [4, 17], and [11] indicated that there was a correlation between the sulfur and mercury contents in the investigated coal samples. The authors pointed out that the mercury content in the samples was clearly correlated with the concentration of sulphides. The correlation was also strongly linked to the type of sulfur and the mercury content in coal samples decreased in the following order: sulfur pyrites sulfur associated with sulphates total sulfur content organic sulfur [11, 17]. An interesting conclusion was the information that some low sulfur coals contain quite high concentrations of mercury, probably due to magma-related intrusions [10, 17]. For those coals significant amount of mercury was found to be associated with organic compounds. However, the authors narrowed their investigation to the coals containing very high amount of sulfur and thus the results for 'low-sulfur' coals are still unknown.

The comprehensive research on the mercury content in the coal samples is relatively new since it was started in the 1970s when the U.S. Geological Survey (USGS) launched a program associated with investigation of the U.S. coal resources [14]. The studies were carried out for almost all the coal and lignite deposits in the U.S. and the determination of the mercury content in American coals was a part of that program. The data allowed to establish one of the most complete databases where the information on mercury content in several coal samples was given. The results indicated that mercury content in the coal varied significantly not only for various coal basins but also between individual mines in each of the basins. The data, collected and published, e.g., by Toole and O'Neil [14] indicated that among U.S. coals the highest mercury content (roughly $0.22 \mu\text{g/g}$) was determined in the lignite samples from the Gulf Coast basin while the lowest values, roughly $0.08 \mu\text{g/g}$, were measured in the samples from the basin of San Juan Unita. The comparison of the mercury concentration in some chosen samples is shown in Table 1.

The average mercury content in Chinese coals is roughly $500 \mu\text{g/g}$ as reported by Liu et al. [10]. The values are much higher than the American data published, e.g., by [17] or [12]. Liu et al. [10] also reported that the range of mercury content in the coal samples is quite wide, roughly $0.16\text{--}1.76 \text{ ppm}$. Those data, however, are not complete since they were obtained from the coals of the Yanzhou basin in Shandong Province only. The level of mercury in that area was higher than determined for some other coals (e.g. from Northern China where the Hg content varied between 0.01 ppm and 5 ppm , with an average of 0.17 ppm [10]).

Table 1. Mercury contents in some chosen coals [14]

Coal type	Minimum $\mu\text{g/g}$	Maximum $[\mu\text{g/g}]$	Average $[\mu\text{g/g}]$
Appalachian	0,003	2,9	0,20
Eastern Interior	0,007	0,4	0,10
Fort Union	0,007	1,2	0,13
Green River	0,003	1,0	0,09
Hams Fork	0,02	0,6	0,09
Gulf Coast	0,01	1,0	0,22
Pennsylvania anthracite	0,003	1,3	0,18
Powder River	0,003	1,4	0,10
Raton Mesa	0,01	0,5	0,09
San Juan River	0,003	0,9	0,08
South West Utah	0,01	0,5	0,10
Uinta	0,003	0,6	0,08
Western Interior	0,007	1,6	0,18
Wind River	0,007	0,8	0,18
Donetsk-Makeevsky	0,17	3,09	0,99
Krasnoarmeesky	<0,01	6,0	2,37
Alma-Marievsky	<0,01	8,40	0,12
Charabowska area	0,40	1,30	0,88

The information on the mercury concentration in Australian coals is quite poor; the average value reported for those coals was roughly 60 ng/g [13].

The coals mined in South Africa are mainly bituminous and are mined in the vicinity of Witbank, Highveld, Waterberg and Sasolburg. As reported by Dąbrowski et al. [3] those coals contain on average 0.04–0.327 ppm of mercury.

Yudovich et al. [16] reported that the content of mercury in Russian and Ukrainian coals was very high, and the mercury content in Russian Pacific coals was up to 15 ppm. The majority of coals from the Donbas basin contained between 0.12 ppm and 2.37 ppm of mercury, but for some samples the values of almost 60 ppm were measured [16]. Similar values were also confirmed by Kolker et al. [9] who reported that the Donbas coals contained 0.02–26 ppm of mercury.

As reported by [16] the mercury content in coals mined in the eastern part of Germany was between 0.16 and 1.5 ppm with an average of 0.33 ppm.

Despite the fact that Poland is one of the largest coal producers in the world and coal still plays an important role in the Polish power generation sector the mercury content in Polish coals has been still quite poorly investigated. Some research in that area was conducted by Kobylecki et al. [19, 20], Wichliński, et al. [21], Bojarska et al. [2], and Hławiczka et al. [8]. The authors [19] reported that the mercury concentration in the coal samples was below 200 ng/g. Bojarska et al. [2] confirmed this value and reported that the average mercury content in their coals was 141 ng/g. Contrary to those authors Hławiczka

et al. [8] reported higher values, up to 396 ng/g. The authors [8], however, investigated only the mercury content in the coals burned by individual households. The mercury content in over 800 coal samples was also examined by Wojnar and Wisz [15] and they reported an average mercury content of roughly 100 ng/g for hard coals and 250 ng/g for lignite samples.

EXPERIMENTAL

The analysis of the mercury content in Polish coals was performed with the use of LUMEX RA-915+ spectrometer coupled with an add-on device RP-91C (Fig. 1). The operation principle of the spectrometer is shown in Fig. 1.



Fig. 1

The determination of the mercury content in the samples was based on Zeeman differential atomic absorption spectrometry with use of high frequency modulation of light polarization and with no need to accumulate mercury on a gold sorbent. The measurement setup enabled to determine the mercury content in gases and liquids, as well as in the solid samples.

In order to determine the mercury concentration in coals the spectrometer was coupled with the add-on device RP-91C and the PC. The role of the add-on device was to provide the conditions for thermal destruction of the sample and reduction of the sample mercury to Hg^0 , as well as its evaporation to the gaseous phase. Since the sample was decomposed at over 800°C the mercury compounds were completely evaporated and the mercury content in the gas could be then analyzed online by the spectrometer RP-915+. The measurements could be conducted for mercury concentration up to 10000 mg/kg with a maximum error of $\pm 20\%$ [28].

The investigations were carried out for coals used as fuel at Polish large-scale power generating facilities. The hard coal and lignite for analysis (total: 63 samples) were taken and delivered to the Czestochowa University of Technology by 41 individual mines. Samples of coals, which examined the mercury content has been provided by individual mines. Since some of the mines did not agree to link their names with the corresponding mercury concentration in coal, the fuel samples for the present analysis were numbered.

The difference between the number of samples and the number of mines was due to the fact that some mines provided a few assortments of coals of different particle size. Some mines (6) delivered also the coal samples before and after the enrichment process that took place 'at the plant'.

For each of the coal samples the detailed investigation was performed and the mercury concentration was measured at least 16 times. Regardless of the mercury content a detailed ultimate and proximate analysis of each of the coal samples was also carried out.

RESULTS AND DISCUSSION

The relationship between mercury and fixed carbon content is shown in Figure 2. Since the increase of the fixed carbon brings about the decrease of the mercury content the results indicate that mercury compounds in those coals are probably bound to mineral matter.

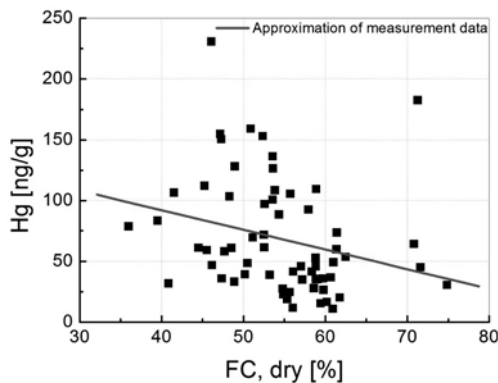


Fig. 2

Figure 3 shows the relationship between ash and mercury content in the coal samples. The mercury content is proportional to the ash content and the ash values were from 4 to 40%.

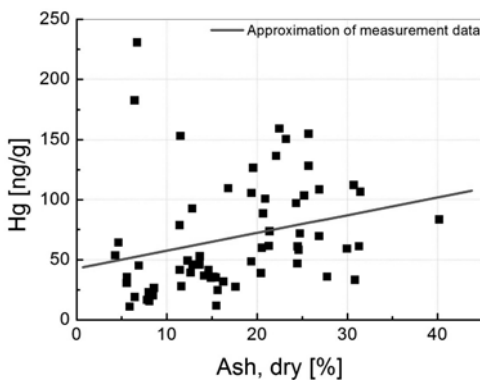


Fig. 3

The mercury content vs. volatile matter is plotted in Fig. 4 for the volatile matter in coal is between 17 and 53%. Despite the fact that the volatile matter varies over a wide range (17%–50%) no direct and simple correlation between those parameters can be established.

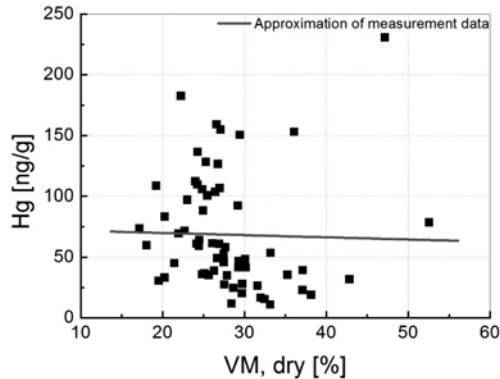


Fig. 4

A higher heating value of the coal samples vs. mercury concentration is plotted in Fig. 5. The high heating values for hard coals were determined at roughly 20–34 MJ/kg, while the corresponding values for lignite were significantly lower, roughly 16–18 MJ/kg. As it is seen in Fig. 5, it is quite difficult to correlate those parameters. The relationship is quite random and probably associated with ash structure and morphology. That phenomenon requires, however, some further and more detailed investigations.

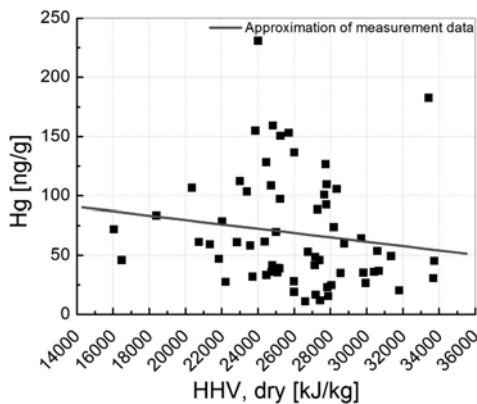


Fig. 5

The mercury concentration versus sulfur content in the coal samples is plotted in Fig. 6. The mercury content increases for higher concentration of sulfur. The results are very interesting and somewhat different to other literature data, e.g., those of Feng et al. [4], where the authors report strong effect of sulfur on the concentration of mercury. The

difference may be associated either with coal types (Feng et al. analyzed only the Chinese coals from Guinzhou province), or the fact that mercury in the Polish coals tested was bound to compounds other than those containing sulfur.

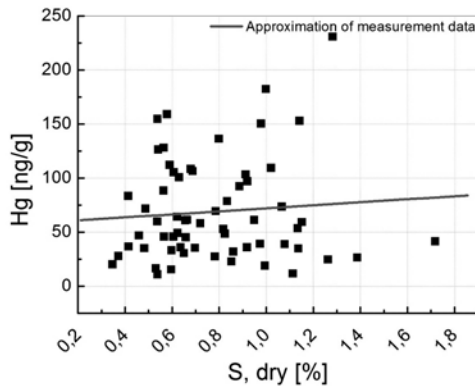


Fig. 6

The results in Figs. 2–6 are summarized in Fig. 7 where the values of the mercury content for all the coal samples are plotted. The results indicate that the lowest and highest mercury contents in the hard coal samples were roughly 13 ng/g, and 156 ng/g, respectively. Both coal samples came from the mines located at the Upper Silesia. The minimum and maximum values for lignite were determined as 79 ng/g and 230 ng/g, respectively, and were higher than the values measured for the hard coals.

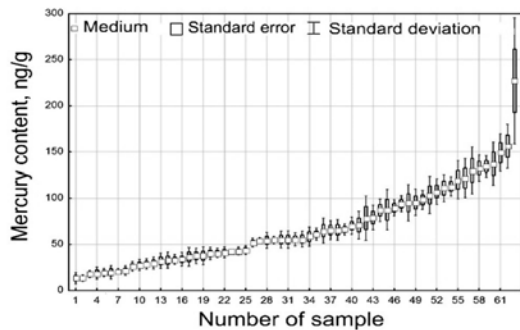


Fig. 7

Figure 8 shows the relationship between the mercury content and the relative number of the investigated coal samples. The results indicate that the largest number of samples, roughly 25%, contained between 40 ng/g and 60 ng/g of mercury. For 21% of the samples the mercury content was determined at roughly 20–40 ng/g, while 3% of the samples contained between 140 ng/g and 160 ng/g of mercury. The summary distribution diagram is shown in Fig. 8.

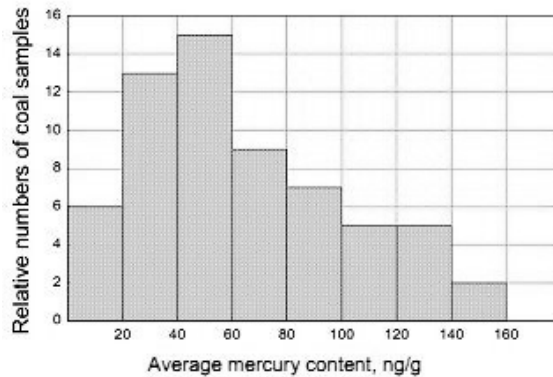


Fig. 8

The effect of the fuel enrichment process on relative mercury content in the samples is presented in Table 2 and Fig. 9. In the case of original coal samples (cf. Table 2) the concentration of mercury was roughly 31–156 ng/g. However, the mercury content for the samples taken at the coal mine after the enrichment process was significantly lower, roughly 28–75 ng/g. The results thus indicate that depending on the coal type roughly 27–74% of the mercury could be removed due to the fuel treatment.

Table 2. Decrease of the ash and mercury content in some chosen Polish coal samples

Coal type	Ash in the sample before the enrichment [%]	Ash in the sample after the enrichment [%]	Ash reduction [%]	Hg in coal before the enrichment process [ng/g]	Hg after enrichment [ng/g]	Mercury reduction [%]
C1	14,6	7,8	46,5	43,06	19,12	55,60
C2	24,5	8,1	67,0	51,87	13,04	74,86
C3	40,2	13,7	66,0	70,25	41,38	41,10
C4	17,6	11,6	34,1	30,93	20,73	32,98
C5	22,5	12,8	42,9	156,13	93,06	40,40
C6	21,3	12,9	39,7	61,13	44,06	27,92

The relationship between the coal ash and mercury content is shown in Fig. 9 for the coal samples before and after the enrichment process. For the majority of the investigated samples the results indicated that the amount of removed mercury was related to the amount of ash that was removed from coal. The different results for the samples C3 and C6 probably indicate that in those cases the majority of mercury was not bound to the ash compounds but rather to organic matrix. Those results are very interesting and require some more detailed studies. The corresponding investigations are currently going on.

SUMMARY

The results of the investigations, reported and discussed in the present paper, may be briefly formulated as follows:

The detailed analysis of a few dozens of Polish coal samples was carried out with respect to their proximate and ultimate analysis, as well as the mercury content. The investigated coals were the main fuels combusted at Polish large-scale power stations.

The mercury content in the investigated hard coal samples was varied from 13.04 ng/g to 156.13 ng/g. In the case of lignite the mercury content was between 78.69 ng/g and 230.41 ng/g. However, the majority of the samples (i.e. almost 50%) contained roughly 20–60 ng/g of mercury.

The results indicated the existence of correlations between the fixed carbon, ash, and mercury content in the coal samples. The decrease of the fixed carbon and ash content brought about the decrease of the mercury content.

No relationship between the volatile matter and mercury in the coal samples was determined. Furthermore, the correlation between mercury content and the HHV of the coal samples was quite vague. The results indicated, however, the existence of a correlation between the sulfur and mercury content but it was weaker than reported in the literature.

The processes of fuel enrichment and getting rid of the ash bring about the removal of significant amount of mercury. In the case of the investigated coal samples up to 75% of mercury was removed from the fuel.

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RTEĆ W POLSKICH WĘGLACH

W niniejszej pracy przedstawiono wyniki badań zawartości rtęci w polskich węglach kamiennych i brunatnych. Wyżej wymienione paliwa są głównymi paliwami używanymi do produkcji energii elektrycznej w Polsce. Wyniki wykazały, że średnia zawartość rtęci w badanych próbkach węgla wynosi około 100 ng/g. Oprócz badań zawartości rtęci przeprowadzono także analizę techniczną i elementarną próbek węgla. Zestawiono zależności pomiędzy zawartością rtęci a zawartością popiołu, fixed carbonu, części lotnych, siarki oraz ciepłem spalania. Przedstawiono także wyniki badań wpływu wzbogacania węgla na zawartość rtęci. Stwierdzono, że w wyniku procesu wzbogacania możliwe było usunięcie prawie 75% rtęci zawartej w wyjściowym paliwie.