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MERCURY IN BITUMINOUS COAL USED IN POLISH POWER PLANTS

RTĘĆ W WĘGLACH KAMIENNYCH SPALANYCH W POLSKICH ELEKTROWNIACH I ELEKTROCIEPŁOWNIACH

Poland is a country with the highest anthropogenic mercury emission in the European Union. According to the National Centre for Emissions Management (NCEM) estimation yearly emission exceeds 10 Mg. Within that approximately 56% is a result of energetic coal combustion. In 121 studied coal samples from 30 coal mines an average mercury content was 112.9 ppb with variation between 30 and 321 ppb. These coals have relatively large contents of chlorine and bromine. Such chemical composition is benefitial to formation of oxidized mercury Hg^{2+} , which is easier to remove in Air Pollution Control Devices. The Hg^r/Q_i^r (mercury content to net calorific value in working state) ratio varied between 1.187 and 13.758 g $Hg \cdot TJ^{-1}$, and arithmetic mean was 4.713 g $Hg \cdot TJ^{-1}$. Obtained results are close to the most recent NCEM mercury emission factor of 1.498 g $Hg \cdot TJ^{-1}$. Value obtained by us is more reliable that emission factor from 2011 (6.4 g $Hg \cdot TJ^{-1}$), which caused overestimation of mercury emission from energetic coal combustion.

Keywords: mercury, bituminous coal (hard coal), emission factor, combustion, power industry

Polska jest krajem o największej antropogenicznej emisji rtęci w Unii Europejskiej. Według najnowszych szacunków KOBiZE roczna emisja rtęci przekracza 10 Mg, w tym około 56% stanowi emisja ze spalania węgla w sektorze produkcji energii. W przebadanych 121 próbkach węgla kamiennego pochodzących z 30 kopalń zaopatrujących polskie elektrownie i elektrociepłownie średnia zawartość rtęci była równa 112,9 ppb, przy zakresie zmienności od 30 do 321 ppb. Węgle te zawierały stosunkowo dużo chloru (średnia 0,241%, przy zakresie zmienności od poniżej 0,05 do 0,45%) i bromu (średnia 14,8 ppm, przy zmienności od 1 do 38 ppm). Taki skład chemiczny sprzyja powstawaniu w spalinach rtęci utlenionej Hg²⁺, która jest łatwiejsza do usunięcia w procesach oczyszczania spalin. Wartość stosunku Hg^r/Q^r_i (zawartość rtęci do wartości opałowej w warunkach roboczych) w badanych węglach zmieniała się w granicach 1,187+13,758 g Hg·TJ⁻¹, a średnia arytmetyczna była równa 4,713 g Hg·TJ⁻¹. Biorąc pod uwagę, że w układ oczyszczania spalin usuwa średnio 46% rtęci dla kotłów pyłowych i 88% dla kotłów fluidalnych, uzyskana w badaniach wartość koreluje ze stosowanym w ostatnich raportach KOBiZE

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wskaźnikiem emisji równym 1,498 g Hg \cdot TJ⁻¹. Wartość ta jest bardziej wiarygodna w porównaniu ze stosowaną do roku 2011 i równą 6,4 g Hg \cdot TJ⁻¹, która była powodem przeszacowywania wielkości emisji ze spalania węgla kamiennego w energetyce.

Słowa kluczowe: rtęć, węgiel kamienny, wskaźnik emisji, spalanie, energetyka

1. Introduction

According to the US Environmental Protection Agency (US EPA) mercury and its vapors are classified as Hazardous Air Pollutants (HAPs) (US EPA, 1997; 1998). In natural environment mercury is present in trace amounts, but due to its toxicity it pose a threat to human life and health (Lippmann, 2009; Commission, 2004). Worldwide studies commissioned by United Nations Environment Programme (UNEP) confirmed harmfulness of mercury and they justify taking actions on international scale (UNEP, 2013). Estimated data shows that in 2005 approximately 1930 Mg of mercury was emitted worldwide (Pacyna et al., 2009). Main sources of mercury emission were: coal combustion (45%), gold production (30%), steel industry (9%), cement plants (7%), waste incineration plants (6%) and production of chlorine and alkali together with crematories (3%).

Poland is a country with highest yearly mercury emission in Europe. This emission is estimated from 14.5 Mg to nearly 20 Mg (Krajowa Inwentaryzacja, 2011; KOBiZE, 2011). This sets Poland among so called 'big emitters', whose yearly emission exceeds 10 Mg. The main source of mercury emission in Poland is energy fuel combustion, mainly coal and lignite with share of approximately 64%. According to the National Centre for Emissions Management (NCEM) Poland emitted 15 653.9 kg of mercury in 2008 and 14 549.3 kg in 2009. Almost 60% (8 565.2 kg) of mercury emission originated from combustion processes and energy conversion. Data from 2009 indicate that mercury emission from professional power and cogeneration plants reached 7 683.1kg. This includes 5 629.4 kg and 1 977.3 kg from combustion of bituminous coal and lignite, respectively (KOBiZE, 2011). Scale of emission for stock taking purposes is based on emission factors developed by Institute for Ecology of Industrial Areas. These factors were 6.4 g Hg · TJ⁻¹ for bituminous coal and 4.0 g Hg · TJ⁻¹ for lignite (KOBiZE, 2011; Hławiczka et al., 2011; Krajowa, 2011). In the most recent report KOBiZE set new mercury emission factors for bituminous coal (1.498 g Hg \cdot TJ⁻¹) and lignite (6.906 g Hg \cdot TJ⁻¹). Reported Polish emission based on new emission factors was 10 115.8 kg of mercury in 2010 and 10 020.1 kg in 2011. Approximately 56% was a result of energy coal combustion: 5 640.4 kg and 5 615.0 kg for 2010 and 2011, respectively (KOBiZE, 2013; Krajowy bilans, 2013).

In Polish bituminous coals mercury content varies between 25 and 300 ppb, whereas in Polish lignites between 100 and 450 ppb (Wojnar & Wisz, 2006; Wichliński, 2011; Wydział, 2011). By comparison, the average mercury content in bituminous coals and lignites combusted in US power plants are: 171 ppb for lignites, 69 ppb for subbituminous coals and 81 ppb for bituminous coals (US EPA, 2002).

In China, in which anthropogenic mercury emission is highest in the World, energetic sector burn coals with average mercury content of 144 ppb. Content varies for specific power plants from 10 to 385 ppb (Zhang et al., 2008; Wang et al., 2010). Estimated yearly mercury emission originating from coal combustion in China varies from 161.6 to 219.5 Mg (Wang et al., 1999; Streets et al., 2005; Jiang et al., 2005).



During coal combustion number of chemical reactions occur resulting in decomposition of compounds containing mercury. As a result in flue gases with temperature above 927°C only vapor of metallic mercury (Hg⁰) is present (Gostomczyk et al., 2010; Gale et al., 2008). Cooling down the flue gas below 540°C allows oxidation of mercury by other compounds such as NO₂, HCl, SO₂ and fly ashes (Nguyen et al., 2008). Share of Hg^0 and its oxidized forms (Hg^+ or Hg^{2+}) in total amount of mercury in flue gases is called mercury speciation. The mercury speciation is crucial for lowering its emission to the atmosphere. Oxidized mercury tend to adsorb for example on fly ashes, which are eliminated by electrostatic precipitators and fabric filters. Due to good solubility in aqueous solutions, oxidized mercury is also removed by Wet Flue Gases Desulfurization (WFGD). Practically all metallic mercury vapor is emitted to atmosphere (Galbreath & Zygarlicke, 2000; Wang et al., 2010; Chmielniak et al., 2010).

Industrial research results confirm that mercury emission to the atmosphere depend on several factors (Hall et al., 1991; Galbreath & Zygarlicke, 2000; Gerasimov, 2005; Zhang et al., 2008). These include: mercury content and chemical composition of combusted coal, type of boiler, mercury speciation of flue gases leaving boiler, types and efficiency of exhaust gas purification processes and presence of specified components in fly ashes and flue gases.

In this work results of studies on mercury content in coal are presented. Over 120 coal samples from 30 different Polish coal mines were examined. Except routine proximate analysis, also content of sulfur, chlorine and bromine were measured.

Experimental 2.

2.1. Acquisition of coal samples

Coal samples were acquired from supplies to 12 power plants and 3 cogeneration plants in Poland (121 samples from 30 different coal mines were taken in total). Samples were acquired automatically from conveyor belts in motion according to Polish Standard PN-90/G-04502. Each sample represented batch of coal of total mass ranging from 1400 to 4200 Mg. From preliminary samples the laboratory samples were prepared for which external moisture was determined according to Polish Standard PN-80/G-04511. Sealed samples were taken to laboratory for analysis. Scope of analysis is described in point 2.2. Scheme of sample acquisition is shown in Fig. 1.

2.2. Coal samples analysis

Air dried samples were prepared according to Polish Standard PN-90/G-04502. The scope of analysis included:

- a) gravimetric method of moisture content determination in analytical sample according to Polish Standard PN-80/G-04511,
- b) gravimetric method of total moisture content determination according to Polish Standard PN-80/G-04511.
- c) gravimetric method of ash content determination according to Polish Standard PN-80/G-04512,
- d) gross calorific value determination and net calorific value calculation according to Polish Standard PN-ISO 1928:2002,

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Fig. 1. Coal sampling scheme

- e) high temperature combustion and detection in infrared method of total sulfur content determination according to Polish Standards: PN-G-04584:2001 and PN-G-04571:1998,
- f) combustion in bomb calorimeter with Eschka mixture and potentiometric titration method of chlorine content according to Polish Standard PN-G-04534:1999,
- g) bromine content with X-ray spectrometry with wavelength dispersion using sequential spectrometer PROMUS II (Rigaku) according to own research procedure. Spectrometer was calibrated with series of synthetic standards with cellulose-graphite matrix. In order to achieve low bromine concentrations in standards potassium bromine was added in graphite solution diluted 1:100. Samples for an X-ray measurements were prepared compression of grounded material in crushing mill (HERZOG). Grain size was below 30 mm and pressure was 200 kN,
- h) mercury content with absorptive atomic spectrometry with cold vapor (CV-AAS) generation in automated mercury analyzer MA-2 (Nippon Instruments Corporation).

Values of these parameters were determined in analytical state (air dried) of sample and afterwards recalculated to states: dry and as received of samples according to recalculating equations from Polish Standard PN-91/G-04510.



2.3. Statistical assessment

Results for analytical samples were recalculated to working state. The following statistics were calculated for each parameter of studied coals:

a) Arithmetic mean \overline{x} :

$$\overline{x} = \frac{\sum_{i=1}^{n} x_i}{n} \tag{1}$$

where:

 x_i — result for single sample,

- n number of samples from given coal mine
- b) minimal value x_{\min} ,
- c) maximal value x_{max} ,
- d) difference between minima and maxima value R,
- e) standard deviation SD:

$$SD = \sqrt{\frac{\sum_{i=1}^{n} (x_i - \bar{x})^2}{n-1}}$$
(2)

f) variability coefficient CV:

$$CV = \frac{SD}{\bar{x}} 100\%$$
(3)

g) expanded uncertainty $U(\bar{x})$ at 95% confidence level:

$$U(\overline{x}) = \sqrt{\left(\frac{1}{n}\right)^2 \cdot \sum_{i=1}^n U^2(x_i)}$$
(4)

where: $U(\bar{x})$ — expanded uncertainty for single result.

2.4. Reliability assessment of achieved results

For quantitative reliability assessment of results and calculated mean values the expanded uncertainty at 95% confidence level was used.

Measure of reliability for single analytical sample examination is results uncertainty $U(X^r)$ considered as uncertainty including: acquisition of preliminary samples, preparation of general sample, separation of analytic and laboratory samples and the analysis itself. Detailed procedure was described in previous work (Burmistrz et al., 2008).

Uncertainty of result recalculated to working state was calculated according to following formula:

$$U\left(X^{r}\right) = U\left(X^{a}\right) \cdot \sqrt{\left(\frac{100 - W_{ex}^{r}}{100}\right)^{2} \cdot U^{2}\left(X^{a}\right) + \left(-\frac{X^{a}}{100}\right)^{2} \cdot U^{2}\left(W_{ex}^{r}\right)}$$
(5)

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where:

- $U(X^r)$ expanded uncertainty of single measurement recalculated to working state of sample,
- $U(X^a)$ expanded uncertainty of single measurement in analytical state of sample,
 - X^a value of single measurement in analytical state,
 - W_{ex}^{r} transient moisture content in tested sample of coal, %.

Uncertainty of mean value of each parameter was calculated according to the formula (4).

To determine the reliability of the average content of mercury in coals from different mines, the estimation error for each mean value was determined (half of the 95% confidence interval) $B_{1/2}$ from the formula:

$$B_{1/2} = t_{\alpha,k} \frac{SD}{\sqrt{n}} \tag{6}$$

where: $t_{\alpha,k}$ — value of Student's *t* distribution at 95% confidence level and k = n - 1 degrees of freedom.

Results 3.

Table 1 presents characteristics of coals from different mines.

TABLE 1

Coal mine Number of samples SD(Hg) CV(Hg) U(Hg) min max W_{ex}' Wa Сľ B_{1/2} \mathcal{Q}_{s}^{a} W,' Ηg A^{a} S_t^a Ē Hg^{a} Hg^{a} % % % % MJ/kg % % % ppm ppb ppb ppb ppb ppb ppb 1 4 9.1 2.7 11.5 12.3 28.509 1.10 0.010 9.8 14.2 13.6 4 68 60 80 10 2 2 7.9 9.1 22.7 26.252 0.68 0.200 12 90 20 1.4 70 110 20 60.8 27.740 3 3 7.7 4.8 12.1 10.2 0.37 0.010 2 80 40 130 14 46 57.5 84.5 4 9.4 0.9 10.2 17.8 28.282 0.63 0.220 17 80 110 10 25.0 20.0 6 60 20 5 5 3.2 4.7 17.8 27.433 1.08 0.140 5 123 100 150 25.3 1.6 18 22 18.1 2.1 23.244 0.72 0.130 9 70 150 14 6 6 5.8 7.8 26.9 114 38 34.9 38.0 7 5.9 2.5 8.2 24.4 24.399 0.58 0.300 24 321 200 550 144 44.9 264.6 3 36 5 9.4 15 7.9 18.4 8 8.2 1.4 26.1 24.792 1.01 0.240 203 168 220 28 16 9 1.4 8.3 31.5 22.392 0.81 0.170 123 4 7.0 18 80 145 16 31 25.2 43.0 2.7 26.700 0.58 0.170 10 3 6.9 9.3 18.6 11 63 50 80 10 15 23.8 27.6 11 7 9.9 1.6 11.3 25.5 24.884 0.80 0.210 10 159 100 180 18 30 18.9 26.8 12 3 8.8 1.6 10.3 22.2 26.000 0.72 0.240 16 127 100 160 20 31 24.4 57.0 13 3 4.8 1.4 6.1 27.3 23.991 0.91 0.250 14 143 130 160 22 15.3 10.7 28.1 14 3 5.2 1.3 6.4 20.7 26.228 0.73 0.170 12 117 100 130 18 15 12.8 27.6 15 5 7.0 1.9 8.8 27.6 23.099 0.59 0.310 20 100 70 140 14 26 26.0 29.9 0.79 16 6 8.5 1.2 9.6 22.6 25.868 0.180 11 171 70 330 28 113 66.1 112.9 17 2 5.5 1.5 6.9 23.2 25.872 0.38 0.280 24 50 50 50 8

Characteristic of coals from different mines



18	11	6.4	1.5	7.8	25.4	24.770	0.89	0.240	14	129	99	160	1.2	1.6	12.4	10.6
19	6	9.3	1.3	10.5	24.4	25.379	0.73	0.230	12	75	50	90	8	14	18.7	14.0
20	6	9.7	2.5	12.0	14.4	27.607	0.61	0.360	31	58	42	80	10	17	29.3	17.0
21	6	7.4	3.0	10.2	17.9	26.492	0.49	0.390	33	30	20	50	4	11	36.7	11.0
22	4	7.2	1.9	9.0	24.0	24.599	1.10	0.300	26	120	110	150	18	20	16.7	27.8
23	3	7.8	2.1	9.8	17.6	26.427	0.31	0.011	1	73	60	90	12	15	20.5	27.6
24	3	9.9	12.9	19.4	12.1	25.200		0.165		79	55	95		20		36.7
24	2	9.8	9.6	18.6	22.8	22.660		0.107		161	148	174		13		39.6
26	2	6.8	5.9	15.3	20.3	24.764		0.481		121	102	140		19		57.8
27	2	9.8	5.9	12.1	21.2	24.451		0.120		68	65	71		3		9.1
28	2	11.3	12.2	20.6	13.7	24.905		0.116		70	57	83		13		39.6
29	2	8.2	3.7	14.7	31.0	21.876		0.168		78	72	84		6		18.3
30	2	5.9	6.3	14.1	26.3	22.586		0.625		148	116	180		32		97.4
	121 ¹	7.7 ²	2.7 ²	10.1 ²	21.9 ²	25.399 ²	0.75 ²	0.219 ²	15.2 ²	112.9 ²	20 ³	550 ⁴				

W – moisture content, A – ash content, Q_s – gross calorific value, S – sulfur content, Cl – chlorine content, Br – bromine content, Hg – mercury content; Upper indexes: r – working state, a – analytical state, 1 – total value, 2 – mean, 3 – min., 4 – max.; Lower indexes: ex – transient, t – total.

3.1. Chemical composition of studied coals

Mercury content in 121 analytical coal samples varied between 20 and 550 ppb (18.5 and 517.6 ppb as calculated for working state). Arithmetic mean was 120.1 ppb (110.3 in working state) and median was 110.0 ppb (99.9 pbb). In majority of samples mercury content was below 200 ppb (Fig. 2). Only in 4 samples originated from one coal mine mercury content exceeded 300 ppb.



Fig. 2. Mercury content in analyzed coal samples (samples arranged according to increasing mercury content)



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Fig. 3 shows results of content analysis of bromine, chlorine and total sulfur. Bromine content in analytical state ranged from 1 to 38 ppm (0.9 to 37 ppm in working state). Average bromine content was 14.8 ppm (13.8 ppm in working state). Only in few samples bromine content exceeded this level.





Fig. 3. Content of bromine, chlorine and sulfur in studied coal samples (samples arranged according to increasing values of parameters)

Chlorine content in analytical samples ranged from 0.05% (below detection limit of the method) to 0.46%. Mean value was 0.241% (0.244% in working state). In over 80% of all samples chlorine content was below 0.30% (8th percentile was 0.28%).

Total sulfur content ranged from 0.29 to 1.37% (from 0.27 to 1.25% in working state) and the mean value was 0.75% (0.69%). For most of coals total sulfur content was below $0.9\% - 8^{\text{th}}$ percentile was 0.90%.

3.2. Mercury content in coal samples

Fig. 4 shows mean mercury content in coals from particular mines. This content varied from 30 to 321 ppb, with mean value for all coal mines of 112.9 ppb. For 25 coal mines mean content value was below 150 ppb. For another 4 coal mines this value ranged from 150 ppb to 230 pbb. For only one mine the mean value was over 300 ppb. For 15 coal mines mercury content was below 100 ppb. For 2 of these mercury content was even lower – below 50 ppb.

Variety of mercury content in samples from particular mines is high (see Table 1). As a consequence of this calculated mean value have significant assessment errors (see Fig. 4). Mean value of assessment error is 43 ppb and variety of this parameter ranges from 9 to 265 ppb. For 10 coal mines assessment error was below 20 ppb, for another 12 below 40 ppb and only in 2 cases exceeds 100 ppb.



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Fig. 4. Mean mercury content in coals from particular coal mines (arranged according to increasing values)

3.3. Mercury emission potential

Mercury emission factors for coal and other fuel combustion are often defined in accordance to fuels net caloric value. Fig. 5 shows values of Hg^r/Q_i^r factors for coals from 30 polish coal mines. Mean value of emission factor was 4.713 g Hg \cdot TJ⁻¹, with variability from 1.187 to 13.758 g Hg \cdot TJ⁻¹. Confidence level of 95% for these coals ranges from 3.815 to 5.611 g Hg \cdot TJ⁻¹. During coal combustion around 98% of mercury is transferred to flue gases. Depending on chemical composition of coal and combustion conditions 10-95% of mercury is eliminated during flue gases purification processes. These include: electrostatic precipitators, fabric filters, wet or semidry desulfurization and selective catalytic NO_x reduction (Wang et al., 1999; US EPA, 2002; Department, 2002; Streets et al., 2005; Jiang et al., 2005; Zhang et al., 2008). Calculated mean mercury reduction ratios for pulverized coal boilers and fluidal boilers were 46% and 88%, respectively. The value of reduction of the mercury content of the flue gas was calculated as the ratio of the content of mercury in the gas after treatment in air pollution control devices (APCD) for the amount of mercury introduced into the boiler with coal. The mean value of mercury emission for pulverized coal boilers is approximately 2.451 g Hg \cdot TJ⁻¹ and 0.566 g Hg \cdot TJ⁻¹ for fluid bed boilers. These values are much lower than factor used by NCEM before 2012 (6.4 g Hg \cdot TJ⁻¹) (KOBiZE, 2011; Hławiczka et. al., 2011; Krajowa, 2011). This value fulfill with the applicable emission factor by NCEM starting in 2012 and amounted to 1.498 g Hg \cdot TJ⁻¹ (KOBiZE, 2013; Krajowy bilans, 2013).

Crucial factor influencing scale of mercury emission is its speciation in flue gases. Speciation depends on chemical composition of combusted coal. In coals with higher chlorine, bromine or other halogen content share of oxidized mercury increases (Zhang et al., 2008; Wang et al.,



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Fig. 5. Mercury emission potential for coals from 30 polish coal mines (arranged according to increasing values)

2009; Wang et al., 2010; Buitrago, 2011). Salts containing these elements decompose during combustion to HCl, HBr and HI and further to Cl₂, Br₂ and I₂. These react with metallic mercury creating: HgCl₂ HgBr₂ and HgI₂. Oxidized mercury is easier to eliminate in dedusting installations as well as in desulfurization processes. Research results show that percentage of mercury removal by electrostatic precipitator increases with logarithm of chlorine content in combusted coal (Streets et al., 2005). Bromine oxidizes mercury at least 10 times more efficient than chlorine (Department, 2002). However, bromine content in coal is 100 to 1000 times lower than chlorine content. There is a correlation between contents of these elements (Fig. 6). Thus, scale of mercury emission from coal combustion is dependent on proportion of mercury content and content of chlorine and bromine. Considering correlation from fig. 6, the scale of mercury emission will be highly dependent on factor Hg/Cl. For particular coal potential mercury emission is correlated with this factor. Fig. 7 illustrates mean values of Hg/Cl for coals from 30 coal mines. For 24 mines this factor is below 0.0001. 13 of them has a factor below 0.00005. Combusting these coals for energy purposes by power plants equipped with flue gases treatment installations will not cause big emission of mercury to the atmosphere. For 4 coal mines with highest Hg/Cl factor (from 0.00056 to 0.0008) the potential of mercury emission is significant. High mercury content and relatively low content of chlorine and bromine causes domination of reduced Hg⁰ form, which will not be eliminated during dedusting and desulfurization processes (Galbreath & Zygarlicke, 2000; Wang et al., 2010; Chmielniak et al., 2010).



Fig. 6. Bromine content vs chlorine content in studied coal samples





485 600 500 Mercury content Hg^a, ppb 300 500 4 100 0 0 5 10 15 20 25 30 35 40 Ash content A^a, % m/m 600 500 Mercury content Hg^a, ppb 400 300 200 100 \$ 4 0 0.0 0.2 0.4 0.6 0.8 1.0 1.2 1.4 1.6 Total sulphur content S_t^a, % m/m

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Fig. 8. Mercury content in relation to chemical composition of studied bituminous coal samples

3.4. Mercury content and chemical composition of coal

Mercury can occur in coal as associated with organic matter, inorganic matter and as free form as so called elemental mercury. In mineral matter mercury is associated with pyrite and sulfates (Zhang et al., 2007). An attempt to correlate quantitatively between mercury content and ash content for studied samples is shown in Fig. 8. No statistically significant correlation between these parameters has been found. However following regularity can be noted: in studied samples among with increasing ash content, mercury content increases. Similar correlation bounds mercury content with total sulfur (see Fig. 8).

4. Conclusions

The average mercury content in analytic samples of coals combusted in Polish power plants was 112.9 ppb with variety ranging from 30 to 321 ppb. Half of coal mines supplied coal with average mercury content below 100 ppb.

Studied coals are characterized by relatively high chlorine and bromine content. During coal combustion they cause mercury oxidation to Hg²⁺ form which easier to eliminate during dedusting and desulfurization processes. For most of studied coals the content ratio of mercury and chlorine was beneficial in terms of decreasing of mercury emission.

An average mercury content indicator related to calorific value was 4.713 g Hg \cdot TJ⁻¹ with error of ±0.898 g Hg \cdot TJ⁻¹ (at 95% confidence level). Due to beneficial chemical composition of coals, significant amount of mercury will be removed during flue gasses treatment at electrostatic precipitators, fabric filters and desulfurization processes. Thus, mercury emission factor will be lower than 6.4 g Hg \cdot TJ⁻¹, which is the value used by NCEM before 2012. This confirms validity of updating mercury emission factor of 1.498 g Hg \cdot TJ⁻¹ after 2012.

With increasing ash content the mercury content increases. This indirectly proves that for studied coals significant amount of mercury is associated with mineral matter. Thus, coal enrichment processes would decrease mercury content in a significant manner. Higher mercury content in coal with higher sulfur content proves that part of mercury is bonded to minerals.

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References

- Belkin H.E., Finkelman R.B., Wang Q., Wang B., Zheng B. 2009. Mercury in China coals. Abstracts of the 21st Annual Meeting of the Society for Organic Petrology, vol. 21, p. 28.
- Buitrago P.A., 2011. Gas-phase Mercury Oxidation: Effect of Bromine, Chlorine and SO₂ under Air Firing and Oxy-fuel Conditions, Experimental and Modelling Study. University of Utah.

Burmistrz P., Bytnar K., Kogut K., Rychcik P., Stelmach S., 2008. Wiarygodność wyników badań węgla kamiennego. Gospodarka Surowcami Mineralnymi, 24, p. 33-48.

- Cao Y., Gao, Z.Y., Zhu J.S., Wang Q., Huang Y., Chiu Ch., Parker B., Chu P., Pan W.P., 2008. Impacts of Halogen Additions on Mercury Oxidation, in A Slipstream Selective Catalyst Reduction (SCR), Reactor When Burning Sub-Bituminous Coal. Environmental Science & Technology, 42, p. 256-261.
- Chmielniak T., Głód K., Misztal E., Kopczyński M., 2010. Mercury Emission from Coal-fired Power Plants. Przemysł Chemiczny, 89, 6, p. 775-778.
- Commission of the European Communities, 2004. Directorate General of Health and Consumer Protection; *Assessment of the Dietary Exposure to Arsenic, Cadmium, Lead and Mercury of the Population of the EU Member States.* Brussels.
- Department of Environmental Protection, 2002. Evaluation of the Technological and Economic Feasibility of Controlling and Eliminating Mercury Emissions from the Combustion of Solid Fuels. Emissions Standard for Power Plants. Boston.
- Galbreath K.C., Zygarlicke C.J., 2000. Mercury Transformation in Coal Combustion Flue Gas. Fuel Processing Technology, 65-66, p. 289-310.
- Gale T., Lani B., Offen G., 2008. Mechanism Governing the Fate of Mercury in Coal-fired Power System. Fuel Processing Technology, 89, p. 139-151.
- Gerasimov G.Y., 2005. *Investigation of the Behavior of Mercury Compounds in Coal Combustion Products*. Journal of Engineering and Thermophysics, 78 (4), p. 668-676.
- Gostomczyk M.A., Jędrusik M., Świerczok A., 2010. Ograniczenie emisji rtęci z procesów spalania węgla. Współczesne osiągnięcia w ochronie powietrza atmosferycznego – POL-EMIS, Polanica Zdrój, 16-19 czerwca 2010, p. 135-144.
- Hall B., Schager B., Lindqvist O., 1991. Chemical Reactions of Mercury on Combustion Flue Gases. Water, Air, Soil Pollution, 56, p. 3-14.
- Hławiczka S., Cenowski M., Fudała J., 2006. Inwentaryzacja emisji niemetanowych lotnych związków organicznych i metali ciężkich za rok 2005. IETU Report, Katowice.
- Jiang J., Hao J., Wu Y., Danid G.S., Duan L., Tian H., 2005. Development of Mercury Emission Inventory from Coal Combustion in China. Environmental Science, 26, p. 34-39.
- KOBiZE, 2011. Poland's Informative Inventory Report 2011.
- KOBiZE, 2013. Poland's Informative Inventory Report 2013.
- Krajowa Inwentaryzacja emisji SO₂, NO₂, CO, NH₃, NMLZO, pyłów, metali ciężkich i TZO za lata 2008-2009 w układzie klasyfikacji SNAP i NFR. KOBiZE, Warszawa, 2011.
- Krajowy bilans emisji SO2, NOx, CO, NH3, NMLZO, pyłów, metali ciężkich i TZO za lata 2010-2011 w układzie klasyfikacji SNAP – Raport syntetyczny. KOBiZE, Warszawa 2013.
- Lippmann M., 2009. Environmental Toxicants Human Exposures and Their Health Effects. Wiley, New Jersey.
- Niksa S., Fujiwara N., 2005. *Predicting Extents of Mercury Oxidation in Coal-Derived Flue Gases*. Journal of the Air & Waste Management Association, 55, p. 930-939.
- Nguyen Y.V., Pessione G.F., 2008. A Three Year Assessment of Mercury Mass Balance from Lambston's Coal Fired Boiler Equipped with FGD and SCR. Power Plant Air Pollution Control Symposium, Baltimore, August 28-31, 2008.
- Pacyna E.G., Pacyna J.M., Sundseth K., Munthe J., Kindbom K., Wilson S., 2009. Global Emission of Mercury to the Atmosphere from Anthropogenic Sources in 2005 and its Future Projection until 2020. MEC6-6th Int. Experts Workshop, Lubliana, Slovenia, 22-24 April, 2009.
- Streets D.G., Hao J., Wu Y., Jiang J., Chan M., Tian H., Feng X., 2005. Anthropogenic Mercury Emissions in China. Atmospheric Environment, 39, p. 7789-7806.
- UNEP, 2013. Mercury. Time to Act; Geneve.
- US EPA, 1998. A Study of Hazardous Air Pollutant Emissions from Electric Utility Steam Generating Units: Final Report to Congress. EPA-453/R-98-004a; US EPA Office of Air Quality Planning and Standards, US Government Printing Office, Washington DC.
- US EPA, 2002. Control of Mercury Emissions from Coal-fired Electric Utility Boilers. Interim Report Including Errata Data, 3-21-02, EPA-600/R-01-109.
- US EPA, 2002. ICR data. http://www.epa.gov/ttn/atw/combust/utiltox/icrdata.xls, January 29, 2002.
- US EPA, 1997. *Mercury Study Report to Congress*. EPA-452/R-97-003; US EPA Office of Air Quality Planning and Standards, US Government Printing Office, Washington DC.

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- Wang Q., Shen W., Ma Z., 1999. The Estimation of Mercury Emission from Coal Combustion in China. China Environmental Science, 19, p. 318-321.
- Wang S.X.L., Zhang L., Li G.H., Wu Y., Hao J., Pirrone N., Sprovieri F., Ancone M.P., 2010. Mercury Emission and Speciation of Coal-fired Power Plants in China. Atmospheric Chemistry and Physics, 10, p. 1183-1192.
- Wang Y., Yufeng D., Yang L., Zhao C., Shen X., Zhang M., Zhuo Y., Chen C., 2009. Experimental Study on Mercury Transformation and Removal in Coal-fired Boiler Flue Gas. Fuel Processing Technology, p. 643-651.
- Wichliński M., 2011. Zawartość i sposoby usuwania rtęci z polskich węgli energetycznych rozprawa doktorska. Politechnika Częstochowska, Wydział Inżynierii i Ochrony Środowiska (praca niepublikowana).
- Wojnar K., Wisz J., 2006. Rtęć w polskiej energetyce. Energetyka, 59 (4), p. 280-284.
- Wydział Energetyki i Paliw AGH, 2011. Wyniki analiz polskich węgli kamiennych i brunatnych wykonanych przez pracowników Wydziału Energetyki i Paliw AGH. Kraków (praca niepublikowana).
- Zhang L., Zhuo Y., Chen L., Xu X., Chen Ch., 2008. Mercury Emission from Six Coal-fired Power Plants in China. Fuel Processing Technology, 89, p. 1033-1040.
- Zhang C., Chen G., Yang T., Guoging L., Mak C., Kelly D., Xu Z., 2007. An Investigation on Mercury Association in an Alberta Sub-bituminous Coal. Energy & Fuels, 21, p. 485-490.