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COAL CLEANING VERSUS THE REDUCTION OF MERCURY AND OTHER TRACE ELEMENTS' EMISSIONS FROM COAL COMBUSTION PROCESSES

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Abstract: Samples of steam coal used in heat and power plants as well as densimetric fractions obtained on a laboratory scale by dense organic liquid separation have been examined. The contents of ash, mercury, chromium, cadmium, copper, nickel and lead have been determined in coal, in the light and medium fraction as well as in the refuse. The degree of removal of mineral matter and the examined heavy metals as well as the coal combustible parts yield have been determined. Examination of 5 coals revealed that it is possible to remove 41% of mercury and more than 35% of other heavy metals bound to mineral matter in coal.

INTRODUCTION

The cleaning of coal, which has been known for a long time and used for the needs of coke industry, is the first stage of the cycle of technologies included in the common programme Clean Coal Technology, the aim of which is to develop new and improve the already existing coal use technologies that are able to meet ecological requirements. The above mentioned first stage includes pre-combustion cleaning of coal through the removal of useless components of mined rock, such as gangue, interlayers containing large amounts of mineral matter and pyrite by applying gravity separation in a water medium. Apart from classic methods, there are also methods of ultra cleaning, which allow ultraclean coals to be obtained. Most domestic heat and power plants burn power fines containing 18–25% of ash, while the process of cleaning enables the content of ash to be reduced below 12%. The usability of coal for power generation purposes drops as the content of mineral matter in coal increases. Investment expenditures for the construction of power blocks fired with coal grow by 0.5% (as converted into an installed power unit) if the content of ash in coal burned increases by 1 g/MJ. Combustion of coals with a high content of ash causes greater wear of power generating equipment, starting with coal mills, through increased wear of water and steam heaters, overload of ash and slag removing plants, drop in the efficiency and availability as well as increased

costs of boiler and auxiliary equipment maintenance, and finishing with a greater negative environmental impact caused by the refuse. Therefore, there are plans to include all the coal produced for the domestic coal-based power industry in the process of cleaning [3]. The favourable environmental effect of burning cleaned coal is manifested in a reduced release and transfer of numerous trace elements into the environment. More and more attention is being paid to the hazard caused by substances which, despite the fact that they are released in small amounts, pose a threat to human populations due to their toxic properties. In the USA 12 elements found in coal, usually in trace amounts, have been deemed by US EPA as (Hazardous Air Pollutants (HAPs): Sb, As, Be, Cl, Cr, Cd, Co, Mn, Ni, Pb, Se and Hg [9]. Toxic properties of mercury and their influence on human health as well as mercury mobility in the environment make it a global problem. Mercury, apart from lead and cadmium, is included in a group of priority pollutants in numerous research projects. In the global emission of mercury from natural and anthropogenic sources, estimated at 5207 Mg/a, the most alarming is the share of the latter, which has been estimated to reach 2320 Mg/a. The largest part of emissions from various areas of human activity – 810 Mg/a comes from power plants fired with fossil fuels [32]. The first programme of mercury emission reduction was born in the USA. Although in the years 1990–1999 the emission of mercury from all anthropogenic sources in the USA was reduced by 45% (from 219.9 to 112.6 Mg/a), the smallest progress was noted in the power engineering sector – by 6% (from 51.1 to 47.9 Mg/a). Therefore, EPA promulgated Clean Air Mercury Rule (CAMR), according to which the emission of mercury in this sector must be reduced to 15 Mg/a in the year 2018. In order to meet the requirements, methods of mercury removal in the pre-combustion process as well as methods of removing mercury and its compounds from flue gas in the post-combustion technology are being taken into consideration. The former methods include the previously applied coal cleaning, which enables removing up to 23% of mercury contained in run-of-mine coal (ROM coal) and the currently developed K-Fuel™ method, which makes it possible to remove ca 70% of mercury from coal by increasing the pressure and heating.

A post-combustion methods include flue gas dedusting and desulphurisation, which by fulfilling their main task – the removal of dust and SO_2 also reduce mercury emissions by means of the cold side electrostatic precipitator – by 36%, and the cold side electrostatic precipitator + wet flue gas desulphurisation scrubber by 80%. A post-combustion method of mercury removal is the activated carbon injection method (ACI), the efficiency of which exceeds 90%.

The cost of mercury emission reduction by post-combustion methods is very high, ranging from ca 10000 to 60000 USD/kg, compared to the cost of reduction of NO_X or SO_2 emission, which reaches 100–200 USD/Mg and 1000–1500 USD/Mg respectively. As a result, the planned project aimed at reducing mercury emissions from power generating plants will cost billions of dollars, although mercury emissions from these plants are only ca 48 Mg. This expenditure is accepted in view of the enormous threat to human health and environment that is posed by mercury emissions [38]. Therefore, studies into simpler methods to be used as major and supporting technologies of mercury emissions reduction are necessary. It has to be emphasised that according to the data provided by EMEP (European Monitoring and Evaluation Programme), the annual emission of mercury into the air from the territory of Poland reached ca 20 Mg [2], which accounted for approximately 10% of mercury emissions in Europe [15–30]. Currently, mercury

emission from anthropogenic sources amounts to 14.6 Mg/a [5]. This data shows that Poland is one of the most mercury contaminated countries in Europe.

TRACE ELEMENTS VERSUS MINERAL MATTER IN COAL

The removal of some trace elements from coal in cleaning processes is possible due to the fact that these elements are to a larger degree bound to mineral than organic matter in coal. As a result, the concentrate obtained in the coal cleaning process contains less mineral matter, and at the same time fewer trace elements. Hence, the manner of trace elements binding in coal has become and still remains the subject of enhanced interest.

The investigations into trace elements bound to organic and inorganic matter in coal were based on observations of changes of their content in high- and low-ash coal and in coal fractions obtained in cleaning processes [6, 11, 14, 21, 37, 40].

In the 1960s and 1970s Zubovic et al. [40] determined the percentage value of trace elements affinity to organic matter in coal for fifteen trace elements contained in coals from the USA (Tab. 1) and found a decreased affinity to coal organic matter in the series: Ge, Be, Ga, V, Cr, Co, Pb, Zn. This means that such elements as: germanium, beryllium and gallium display the greatest affinity to coal organic matter, while zinc is chiefly bound to mineral matter. In the case of the remaining elements subjected to research, different ways of being bound to organic and inorganic matter in coal are observed.

Table 1. Affinity of some trace elements to coal organic matter in selected American coals, in a scale of 0–100, [40]

Element	Affinity to coal organic matter
Ge	87
Be	82
Ga	79
Ti	78
B	77
V	76
Ni	59
Cr	55
Co	53
Y	53
Mo	40
Cu	34
Sb	27
La	3
Zn	0

Finkelman [11], while confirming that the degree of affinity of particular trace elements to coal organic and inorganic matter is different for particular trace elements, linked their presence in coal with relevant minerals in coal inorganic matter (Table 2).

Table 2. Forms of some trace elements' occurrence in coal [11]

Element	Form of occurrence	Evaluation assurance level
Antimony	bound to pyrite, also as an additive in sulphides	4
Arsenic	bound to pyrite	8
Barium	as barite	6
Beryllium	bound to organic matter	4
Boron	bound to inorganic matter	6
Cadmium	in sphalerite	8
Chlorine	occurs in a form of chloride ions in water or adsorbed on macerals	6
Chromium	bound to organic matter or loamy material	2
Cobalt	bound to pyrite and partly as an additive in sulphides	4
Copper	as chalcopyrite	8
Fluorine	in various minerals	5
Lead	as galena	8
Mercury	bound to pyrite	6
Manganese	occurs in carbonates, siderites and ankerite	8
Molybdenum	probably in sulphides	2
Nickel	probably in sulphides	2
Phosphorus	in phosphates	6
Selenium	bound to organic matter, occurs in pyrite, sulphides and selenides	8
Argentum	occurs in various sulphides	4
Thallium	bound to pyrite	4
Thorium	as monazite with a low concentration in xenotime	8
Tin	as tin oxides and tin sulphides	6
Vanadium	present in clay and bound to organic matter	3
Uranium	bound to organic matter, partly found in zircon	7
Zinc	in sphalerite	8

When investigating Polish coals, Parzentny [31] found that inorganic mineral matter clusters are basic carriers of trace elements: Zn, Pb, Cd, Ni, Co, Cu and Cr. There is a correlation between the content of the discussed elements and the content of mineral matter clusters in coal. Another dependence is also observed between the amount of Ni,

Co, Cu and Cr in inorganic mineral matter clusters and the content of loamy minerals as well as between the amount of Zn, Pb, Cd and Ni in coal and the share of pyrite. Moreover, mutual affinity between elements, especially between Co and Ni in the clusters of inorganic mineral matter having a thickness below 5.0 cm was discovered, which indicates similarity of their geochemical properties.

Mercury in coal is usually bound to sulphur in a form of pyrite FeS_2 (65–70%), its small amount also occurs in a form of mercury sulphide HgS, and the remaining part – in organic coal matter [20]. The content of mercury in coal depends on the type of fuel, the origin and share of mineral matter [33]. According to different authors, the level of mercury in Polish hard coal ranges from 50 to 240 ppb, and in brown coal – from 120 to 516 ppb [24]. In the coal cleaning process by the flotation and gravity method, 30 to 45% of mercury can be separated from coal [1], and with more advanced cleaning methods this figure can reach even 60% [39]. Steam coals cleaning in pre-combustion processes reduces the amount of total mercury in flue gases. The notion of total mercury THg includes all its forms Hg^0, Hg^{2+} and Hg_p. It is assumed that the shares of particular forms of mercury released into the atmosphere are as follows: 60% in the form of metallic mercury vapours Hg^0 (TGM – Total Gaseous Mercury), 30% in the form of volatile compounds Hg^{2+} (mainly $HgCl_2$) (RGM – Reactive Gaseous Mercury) and 10% in the solid form of adsorbed dust particulates (TPM – Total Particulate Mercury) [12–35].

In the process of coal combustion, mercury is distributed in the solid products of combustion and flue gas desulphurisation. The data on mercury content in combustion waste indicates that it is mainly contained in fly ash, and only a small amount remains in slag. The authors' own investigations into the distribution of mercury in coal combustion and flue gas desulphurisation products suggest that up to 95% of released mercury is accumulated in gypsum formed in FGD plants by the limestone method [23, 24].

Contemporary investigations are focussed mainly on post-combustion processes. They include mercury removal methods, among others FBC – Fluidized Bed Combustion, which enables utilisation of coal with a high Cl content. From an FBC boiler 4.5% of mercury is released in the form of Hg^0, while 55% of mercury is adsorbed on volatile ash particles [25]. The application of NO_x selective reduction method (SCR) allows for the oxidation of mercury in the form of vapours to the form of Hg^{2+} and the reduction of Hg^0 mercury ranging from 40% to 60% to a level of 2–12%. When combined with flue gas desulphurization technology (FGD), SCR enables the removal of up to 90% of Hg^0 [17]. Also known are sorption methods with active coal injection [13, 26] into flue gas before dedusting in an ESP (Electrostatic Precipitator} [4, 28] or FF (Fabric Filter) [22]. In the first case, the efficiency of mercury sorption reaches 60%, and in the other – 90%. Another technology that deserves attention is the advanced CFA (Circulating Fluidized Bed Adsorber), in which the duration of contact between the gases and the sorbent is longer and the sorbent consumption lower. Better effects are achieved by applying mercury sorption in a stationary bed of active coal (efficiency reaching 90–95%) [16] and by using sulphur impregnated sorbents (efficiency up to 99%) [8] than by injecting active coal dust into flue gases [18]. Wet gas cleaning in scrubbers reduces the emission of mercury, although data on the efficiency is divergent [7, 35]. Particularly effective, reaching up to 70%, is the cleaning of mercury in the Hg^{2+} form. On the other hand, investigations into the use of scrubbers in FGD, which have been carried out in the USA and Germany, prove that oxidized mercury is reduced again to elementary mercury.

Poland is obliged to apply BATs (Best Available Techniques) in order to reduce the emission of pollutants, including mercury release into the atmosphere [19–27]. These methods include the above mentioned mercury sorption on active coal with an addition of sulphur as well as fabric filters and electrostatic precipitators, comprising flue gas desulphurisation processes. Other quoted BATs applied in power fuel combustion include also the removal of mercury before the process of combustion and mercury removal from flue gases.

EXPERIMENTAL

Objective and scope of research

The aim of the investigations is to compare the content of selected trace elements in the concentrate and waste obtained in the process of coal separation in heavy liquids on the laboratory scale. The scope of works included the determination of Cd, Cu, Cr, Hg, Ni and Pb in 5 samples of Upper-Silesian commercial steam coals and in different density fractions that were obtained from these coals.

Methodology

Samples of ROM coal were taken from four power plants in the south of Poland. The grain size class ranging from 0.2 to 1 mm was obtained from the raw coal, which was next separated into following density fractions: of light (<1,3), medium (1.3–1.8) and refuse (>1.8) by applying the dense medium gravity separation method and using organic liquid compounds (solutions of tetrabromoethane in toluene) with densities of 1.3 and 1.8 g/cm^3. The shares of fractions and ash contents were determined.

Mercury content in ROM coal samples and in fractions subjected to cleaning in heavy liquids was determined by means of an MA-2 mercury analyser produced by Nippon Instruments Corporation [23]. The concentrations of Cd, Cu, Cr, Ni and Pb in ROM coal samples and in fractions obtained after separation in heavy liquids were determined in mineralizers by atom absorption spectrometry methods, in the flame variant, using an AVANTA PM spectrometer produced by GBC Scientific Equipment [23].

Research results and discussion

The results of run of mine coal (ROM) separation into fractions by means of heavy liquids in the form of shares of particular fractions have been given in Table 3. The results of determinations of selected metals in ROM coals and fractions have been presented in Table 4.

The mercury distribution in coal densimetric fractions has been presented in the graph (Fig. 1–5) because of its exceptional toxicity.

On the basis of the data on the concentration of a given trace element in ROM coal c_{iROM} as well as the share of refuse S_R in ROM coal and the concentration of a particular trace element in refuse c_{iR}, RE – the efficiency of element removal in the cleaning process was calculated. To this end, the ratio of content of element i in the refuse to the content of element i in ROM coal was calculated according to the following equation:

$$RE = \frac{S_R \cdot c_{iR}}{1 \cdot c_{iROM}} \cdot 100\%$$

Table 3. The shares of densimetric fractions obtained in the coal cleaning process and ash concentration

Fraction [g/cm³]	Power plants									
	Jaworzno III				Siersza		Gliwice		Nowy Wirek	
	coal I		coal II							
	S	Aᵃ [%]	S	Aᵃ [%]	S	Aᵃ [%]	S	Aᵃ [%]	S	Aᵃ [%]
ROM coal	1.000	16.87	1.000	24.99	1.000	11.45	1.000	19.42	1.000	13.28
<1.3	0.053	1.56	0.130	1.35	0.359	2.39	0.510	1.84	0.667	1.23
1.3–1.8	0.772	4.95	0.604	6.91	0.542	5.16	0.299	14.26	0.200	18.60
>1.8	0.175	74.14	0.266	77.49	0.099	78.50	0.192	74.1	0.133	71.67

ROM coal – run-of-mine coal, S – share of fraction

Table 4. Concentrations of heavy metals in coal samples and densimetric fractions

Power plant	Sample	Trace element					
		Cd	Cu	Cr	Hg	Ni	Pb
		ppm			ppb	ppm	
Jaworzno III coal I	ROM coal	2.43	29.38	22.21	59.1	26.35	66.94
	Fraction <1.3	3.31	14.83	25.96	36.7	39.77	35.18
	Fraction >1.8	3.58	88.18	136.97	160.3	84.84	233.47
Jaworzno III coal II	ROM coal	3.36	26.93	38.30	122.9	49.31	229.23
	Fraction <1.3	3.61	11.20	16.76	35.3	25.61	79.28
	Fraction >1.8	3.99	63.95	82.65	148.3	55.47	266.20
Siersza	ROM coal	3.20	14.65	17.60	53.2	32.94	112.69
	Fraction <1.3	3.24	10.20	13.89	11.3	33.94	206.40
	Fraction >1.8	4.81	112.72	500.88	425.0	264.48	296.51
Gliwice	ROM coal	3.18	38.80	37.68	74.9	36.25	109.44
	Fraction <1.3	2.18	17.35	20.81	33.8	33.52	100.32
	Fraction >1.8	3.01	50.48	73.95	105.1	57.42	154.03
Nowy Wirek	ROM coal	3.82	24.10	20.46	28.1	34.18	137.045
	Fraction <1.3	5.04	13.22	11.76	24.6	26.48	207.26
	Fraction >1.8	5.36	56.00	117.22	37.2	80.27	293.42

Table 5. Recovery of combustible parts and efficiency of ash and selected heavy metals removal from coal

Plant	Recovery of combustible parts of the coal (%weight)	Efficiency of removal . %						
		Ash	Cd	Cu	Cr	Hg	Ni	Pb
Jaworzno III Coal sample 1	94.5	77	26	52		47	56	61
Jaworzno III Coal sample 2	92.1	83	32	63	57	32	30	31
Siersza	97.6	68	15	76		79	80	26
Gliwice	93.9	73	18	25	38	27	30	27
Nowy Wirek	94.7	72	19	31	76	18	31	29

Recovery (ε) of coal combustible parts was also calculated according to the following equation:

$$\varepsilon = \gamma \ \frac{(100 - A_{cc})}{(100 - A_{ROM})} \cdot 100\%$$

where:

γ – yield of concentrate
A_{cc} – ash concentration in clean coal [wt %]
A_{ROM} – ash concentration in ROM coal [wt %]

The yield of concentrate in the case of these investigations is the total share $S_{<1.3}$ and $S_{1.3-1.8}$.

Research focused on samples of steam coal – a mix of commercial coals delivered from various coal mines to power plants. The plants differ in their capacity and the type of boilers used. In Jaworzno III, Siersza and Gliwice these are boilers with a pulverised-fuel furnace, with the steam yield reaching 650, 380 and 70 Mg/h respectively. Nowy Wirek is equipped with a mechanical stoker boiler having the power of 5 MW. Coal samples were cleaned in heavy organic liquids so as to avoid contamination with the compounds of trace elements present in liquids used in the process of industrial cleaning or flotation.

Although obtained in laboratory conditions and on a laboratory scale, the results refer to real processes of power coal combustion and ecological effects of these processes.

The investigated coal samples contained 11.45–24.99% of ash, and in the refuse formed due to the cleaning process the ash level reached from 71.67 to 78.50%. In the obtained usable fraction, made up of a light and medium fraction, the content of ash ranges from 4.06 to 6.43%. The majority of ash – 68% to 83% was removed from coal together with the separated refuse. Taking into account the separation of refuse containing mostly mineral matter with a usable fraction, the amount of recovered combustible parts

reached 92.1 to 97.6%. This means that the loss of chemical energy contained in coal in the cleaning process ranges from ca 2.5 to nearly 8%. The concentration of selected trace elements in the examined ROM coals is, as usual, differentiated. It was found that the level of mercury ranges from 28 to 123 ppb, cadmium – 2.4 to 3.8 ppm, copper – 14.7 to 38.8 ppm, chromium – 17.6 to 38.3 ppm, nickel – 26.4 to 49.3 ppm and lead – 66.9 to 229.2 ppm. In five investigated power coals the concentration of mercury did not exceed 122 ppb, which means that it was lower by a half compared to the ROM coal sample examined in the quoted study [1]. In the light fraction separated from these coals the level of mercury ranges from 11 to 37 ppb, cadmium – from 2 to 5 ppm, copper – 10 to 17 ppm, chromium – 12 to 26 ppm, nickel – from 26 to 40 ppm and lead – from 35 to 207 ppm. In the refuse separated from these coals the content of mercury ranges from 37 to 425 ppb, cadmium – from 4 to 5 ppm, copper – from 50 to 113 ppm, chromium – from 74 to 501 ppm, nickel – from 55 to 264 ppm and lead – from 154 to 293 ppm.

The degree of removal (%) of the examined elements calculated from the results of analyses of 5 coals and fractions obtained by cleaning is as follows: 18–79 for mercury, 15–32 for cadmium, 25–76 for copper, 38–76 for chromium, 30–80 for nickel and 26–61 for lead. Therefore, the results are differentiated, which probably results from the fact that particular elements occur in different forms in coal mineral matter. The degree of mercury removal reaching an average of 41% is close to the result obtained by the cleaning methods similar to the ones applied in industrial conditions [1].

The results seem to confirm that steam coal cleaning as a pre-combustion process will considerably contribute to a reduction of contamination of flue gases with mercury and other heavy metals.

This will happen if, according to forecasts, the whole power coal burned in power boilers is cleaned. In order to predict the expected reduction of heavy metals content in the cleaned coal, it is necessary to carry out laboratory investigations into coal which will be delivered in big quantities to power plants, while maintaining the same quality parameters.

The increasing of cleaning degree so as to enhance mercury removal efficiency should be preceded by a detailed economic evaluation, which ought to take into consideration investment costs, M&O costs, the loss of some percentage of energy contained in refuse combustible parts as well as the costs of environmentally safe refuse utilisation. It should also take into account the previously identified savings owing to the use of a cleaner fuel in power plants and, finally, the savings related to the consumption of an adsorbent or other agents used to remove mercury in post-combustion processes.

CONCLUSIONS

Laboratory investigations into the concentration of selected heavy metals in different density fractions obtained in the process of cleaning of five samples of steam coal in organic heavy liquids confirmed the binding of some heavy metals to mineral coal matter. This refers to mercury, copper, chromium, nickel and lead, and to a smaller degree – cadmium. In the examined samples the highest concentration of all the investigated elements was found in the refuse, in coal fractions having a density of >1.8 g/cm^3, with an average content of ash reaching 75.18%, whereas the lowest concentration was observed in coal fractions with density <1.3 g/cm^3, containing an average of 1.67% of ash.

The calculated degree of removal of mineral matter and the examined trace elements is different for various coal samples, which may be accounted for by different properties of mineral matter and macro-elements in coal. The separation of light and medium fractions from coal enables obtaining fuel which contains less mercury than ROM-coals. In the most favourable case it was only 21% of mercury and in the worst case – 82%, of mercury while the average value reached 41% of mercury in the five examined coals. Coal cleaning also enables to remove a significant amount of Cu, Cr, Ni, and Pb. A high degree of removal was achieved for Cu (an average of 49% from 5 coals), Cr (an average of 57% from 3 coals), Ni (an average of 45% from 5 coals) and Pb (an average of 35% from 5 coals). Cleaning in the form of a pre-combustion process causes a slight loss of chemical energy, as the recovery of coal combustible parts reaches an average of 94.6% in 5 examined coals. When evaluating the results, one should bear in mind that a laboratory scale was applied and organic heavy liquids were used for cleaning. An advantage of this procedure was the fact that mercury and other heavy metals were eliminated from investigations and measurements. Whether a more thorough coal cleaning process is justified in order to remove mercury and other heavy metals in a more efficient way should be established on the basis of extensive research in a demonstration scale as well as an economic analysis.
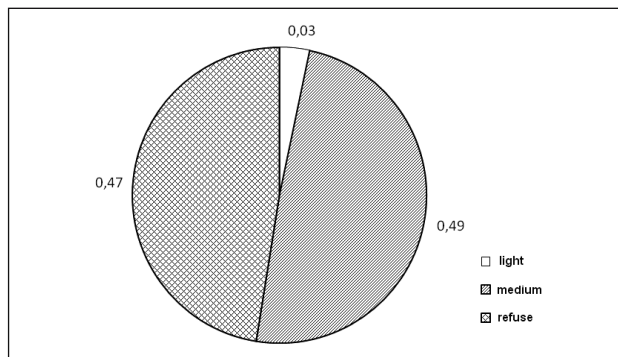

Fig. 1. Distribution of mercury in the densimetric fractions of coal 1 used in Power Plant Jaworzno III
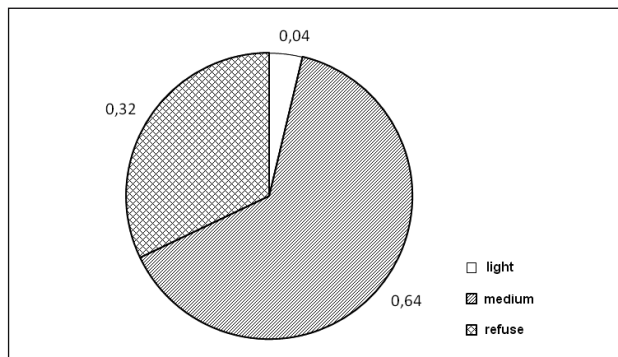

Fig. 2. Distribution of mercury in the densimetric fractions of coal 2 used in Power Plant Jaworzno III
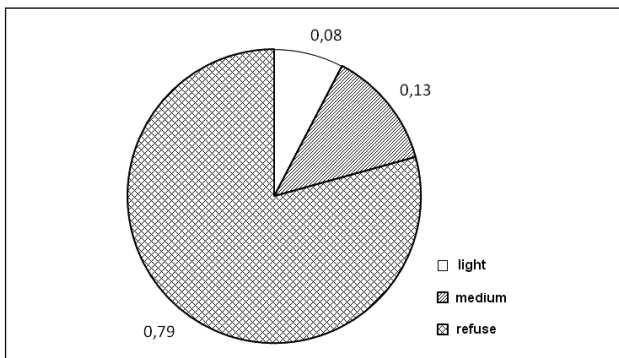
Fig. 3. Distribution of mercury in the densimetric fractions of coal used in Power Plant Siersza
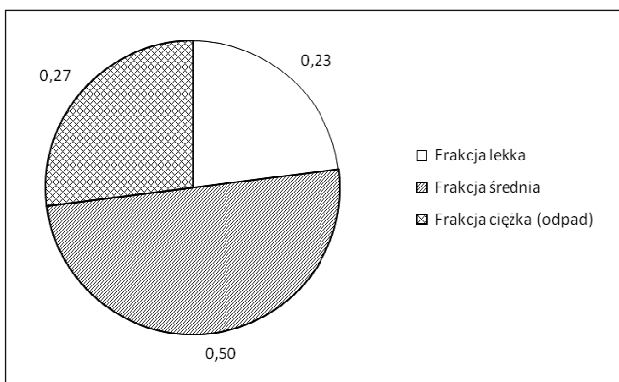

Fig. 4. Distribution of mercury in the densimetric fractions of coal used in Power Plant Gliwice
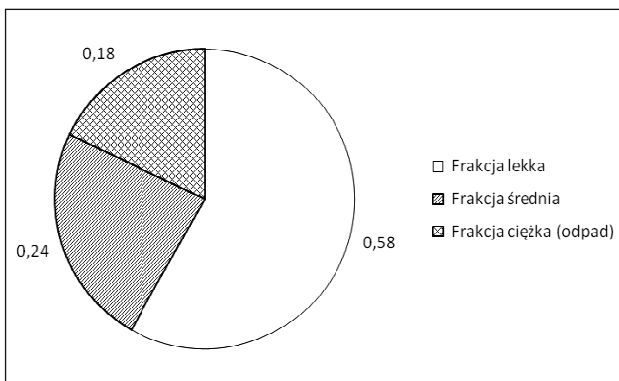

Fig. 5. Distribution of mercury in the densimetric fractions of coal used in Power Plant Nowy Wirek

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