Studies on the Effectiveness of Mercury Removal from Hard Coal with the Rejects in the Washing and Dry Deshaling Processes

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Abstract

Due to the toxicity of mercury a reduction of its emission is the objective of many legislative actions. In the case of power plants, there are well-known methods allowing for the removal of mercury from flue gases (post-combustion). In the case of households and small-scale combustion installations these methods are not used, which is caused by high investment costs. The most effective solution for this group of customers is the removal of mercury from coal (pre-combustion). This can be obtained in the washing and deshaling processes.

The coal-cleaning equipment which is commonly used in Polish coal preparation plants was analyzed, i.e. dense media separators, grain and fine coal jigs, flotation machines, as well as the pneumatic vibrating FGX type separator. The effectiveness of the coal cleaning process was assessed with the use of the RF factor (the ratio of the mercury content in the rejects to the mercury content in the feed coal). The obtained values of the RF factors show that mercury has a tendency to remain in the rejects, while higher values of the RF factors were obtained for the dry deshaling process (from 0.83 to 2.82) than for the washing process (from 0.53 to 2.24).

Keywords: hard coal, washing, deshaling, mercury, removal

Introduction

Mercury is commonly found in hard coal (Ketir & Yudovich 2009) and its combustion is one of the main sources of the anthropogenic mercury emission into the atmosphere (Pacyna et. al 2016). Due to the toxicity of mercury a reduction of its emission is the objective of many legislative actions, among others the BAT conclusion for large combustion plants adopted by the European Commission (BAT-LCP 2017). In the case of the large combustion plants, there are well-known and widely used methods allowing for the removal of mercury from flue gases (the post-combustion stage), among others a sorbent injection into the flue gases stream (Wierońska et al. 2018). In the case of households and small-scale combustion installations these methods are not used. This is caused by both lack of technical possibilities as well as high investment costs. The most effective solution for this group of customers is the removal of mercury from coal (the pre-combustion stage), which can be obtained with the use of various methods (Dziok 2018).

The removal of mercury from hard coal can be achieved, among others, through the cleaning process (Baic & Blaschke 2018, Dziok & Strugała 2017, Dziok 2018). This process yields: (i) clean coal with a reduced ash content and an increased calorific value, (ii) middling products that are used in the power industry, and (iii) rejects. The rejects are directed to a landfill or are used as a substitute for the natural aggregates (Baic & Blaschke 2013). Thus, they are not directed to the thermal processes and, therefore, mercury contained in the rejects is not released into the atmosphere during coal combustion.

The washing equipment is commonly used in hard coal processing plants. Recently, the dry separation methods allowing for the efficient deshaling of raw coal have become more popular. The Authors' scientific works confirmed the possibility of mercury removal from coal in these processes, although the effectiveness of mercury removal together with rejects varied from 8 to 96% (Dziok & Strugała 2017, Dziok 2018). This should be explained by the difference in the mode of mercury occurrence in individual coals. In Polish hard coals mercury is mainly found in pyrite (Dziok et al. 2019), and the effectiveness of mercury removal from coal in the washing processes increases along with the growth in the amount of removed pyrite (Dziok et al. 2015). Effective pyrite removal from hard coal, and, consequently, also mercury removal, may be achieved with the use of the pneumatic vibrating separators (Baic et al. 2014, 2015, Baic & Blaschke 2017, 2017a, 2018, Dziok & Strugała 2017). The aim of the study was to assess the effectiveness of mercury removal from hard coal together with the rejects in the washing and dry deshaling processes.

Methodology

The coal-cleaning equipment which is commonly used in Polish coal preparation plants was analyzed, i.e. dense media separators, grain and fine coal jigs, flotation machines, as well as the pneumatic vibrating FGX type separator. The first four equipment items are used for the washing process and the last one for the dry deshaling process of raw coal.

Fig. 2. Photographic evidence of the device for physical waste treatment – EP 2388068 (electrostatic field, spark discharge, UV radiation)
Rys. 2. Fotografia urządzenia do fizycznej obróbki odpadów – EP 2388068 (pole elektrostatyczne, wyładowanie iskrowe, promieniowanie UV)

Case no.	**Coal-cleaning equipment**	**Particle size [mm]**	**Mercury content Hg^d [µg/kg]**	
			feed coal	**rejects**
1	dense media separators	>20	57	62
2			54	62
3			114	249
4			67	116
5	grain coal jigs	0.5–70	148	79
6			83	71
7	fine coal jigs	0.5–20	99	88
8			75	55
9			131	190
10			134	114
11	flotation machines	<0.5	66	148
12			218	136
13			56	69
14			137	115
15			127	127
16			93	93
17	pneumatic vibrating FGX type separator	0–25	113	319
18			146	121
19			88	162
20			131	132
21			65	78
22			124	160

For each of the analyzed equipment items, the samples of feed coals and rejects were investigated. In all the samples mercury content was determined with the use of the MA-2 analyzer (Nippon Instruments Corporation), based on cold vapor atomic absorption spectroscopy (CVAAS). The measurements were carried out in compliance with the EPA 7473 Method. The obtained results are given in Table 1.

In order to determine the effectiveness of the analyzed processes, the *RF* factor was used. *RF* was calculated as the ratio of the mercury content in the rejects ($Hg_{rejects}$) to the mercury content in the feed coal (Hg_{feed}) – Eq. (1). *RF* values higher than 1 indicate the accumulation of mercury in the rejects and those lower than 1 indicate a lower mercury content in the rejects in comparison to the mercury content in the feed coal.

$$R F \quad \frac{H g}{H g}, [-] \qquad (1)$$

where:
RF – factor of mercury accumulation in the rejects separated from coal in the washing/deshaling processes [-]
$Hg_{rejects}$ – mercury content in the rejects [µg/kg]
Hg_{feed} – mercury content in the feed coal for the coal washing/deshaling processes [µg/kg]

Results and discussion

The mercury content in the feed coals for the coal cleaning process varied from 54 to 218 µg/kg (the average of 106 µg/kg) and was smaller than the mercury content in the rejects separated from coal – from 55 to 319 µg/kg (the average of 125 µg/kg). For the entire population of analyzed samples a significant correlation between the mercury content in the feed coal and in the rejects was not found (Fig. 1a). Such a relationship was obtained only for the dense media separators (Fig. 1b). The significance of the correlation was verified with the use of the F-Snedecor test at the confidence level of 0.95. The lack of correlation for the entire population may be caused by, both, differences in the mode of mercury occurrence in individual coals (Dziok et al. 2015) as well as by differences in mercury content in the grains of pyrite and other sulfides which occur even within a single grain (Dziok et al. 2019). The significant correlation obtained for the dense media separators may indicate that for coarse size fractions of hard coal the dominant mode of mercury occurrence is the adventitious inorganic constituents which undergoes separation very well.

A comparison of mercury content in the rejects derived from the analyzed equipment items is shown in Fig. 2. The highest mercury content and the highest dispersion of results

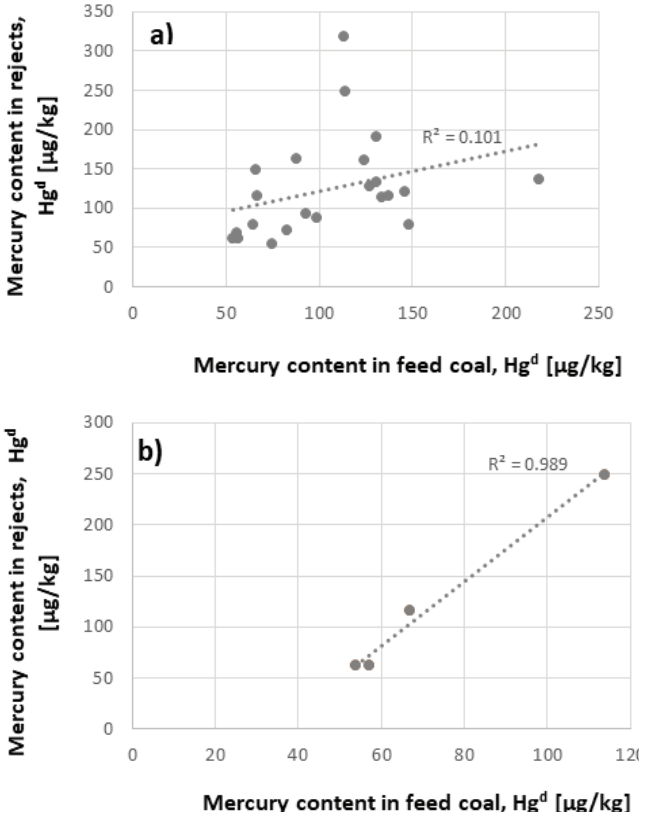

Fig. 1. Relationship between mercury content in feed coal and rejects derived from the coal washing/deshaling processes:
a) all analyzed cases, b) dense media separators

Rys. 1. Zależność między zawartością rtęci w węglu surowym a odpadami pochodzącymi z procesów wzbogacania/odkamieniania węgla:
a) wszystkie analizowane przypadki, b) separatory cieczy ciężkich

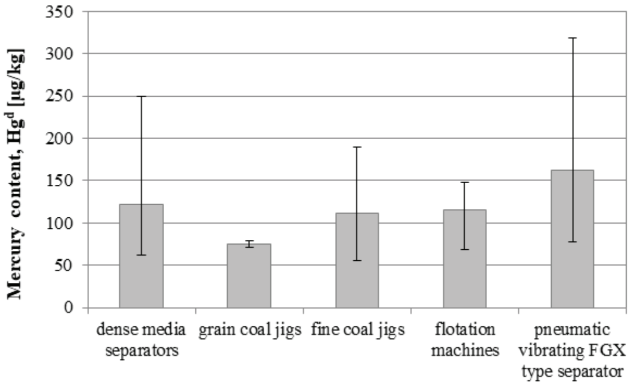

Fig. 2. Comparison of mercury content in the rejects derived from individual equipment items
(the whiskers represent the dispersion of the obtained results)

Rys. 2. Porównanie zawartości rtęci w odpadach pochodzących z poszczególnych urządzeń (wąsy reprezentują rozrzut uzyskanych wyników)

were recorded for the rejects derived from the dense media separators as well as the pneumatic vibrating separators. The lowest values were obtained for the grain coal jigs. In the case of the coal jigs, low mercury content may be related to its accumulation in the middling products, which was pointed out in our previous work (Dziok et al. 2019). The mercury content in the analyzed middling products was 313 and 246 µg/kg (dry basis), respectively. Their examination using an electron probe microanalyzer (EPMA) showed the occurrence of mercury mainly in the grains of pyrite, marcasite as well as chalcopyrite and the mercury content in them reached 0,1%.

In Fig. 3 a comparison of the *RF* values determined for the analyzed equipment items used in the hard coal washing process was presented. The influence of grain size on the mercury content in the rejects is noticeable. Only in the case of dense media separators for each of the analyzed cases the *RF* was higher than 1 (from 1.09 to 2.18 with the average at the level of 1.54). This shows, as previously mentioned, a very good separation of mercury from the raw coal of large grain size in the coal washing process in the dense media separators (coal grain size >20 mm). In the case of the grain coal jigs (coal grain size 0.5–70 mm) for each of the analyzed equipment items the mercury content in the rejects

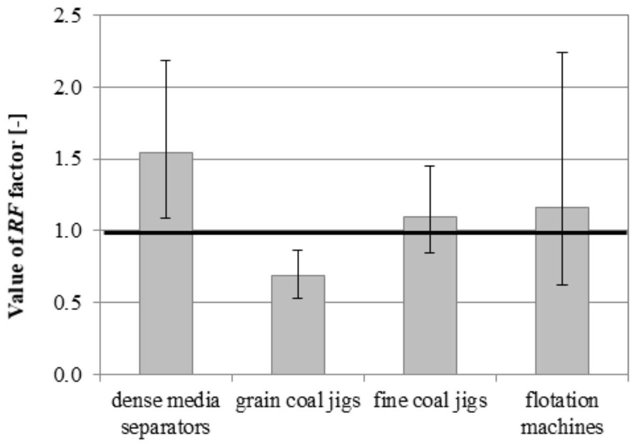

Fig. 3. Comparison of the *RF* values determined for the analyzed equipment items used in the hard coal washing process (the whiskers represent the dispersion of the obtained results)

Rys. 3. Porównanie wartości *RF* wyznaczonych dla wzbogacalników w procesie wzbogacania węgla kamiennego (wąsy reprezentują rozrzut uzyskanych wyników)

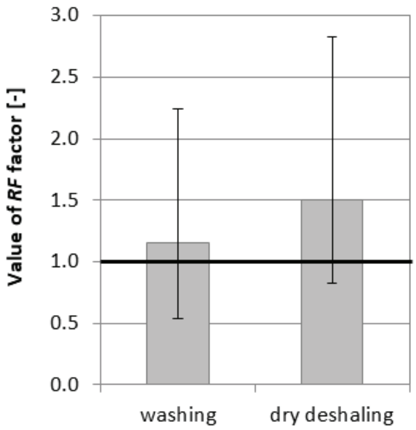

Fig. 4. Comparison of the *RF* values determined for analyzed equipment items used in the hard coal washing and deshaling processes (the whiskers represent the dispersion of the obtained results)

Rys. 4. Porównanie wartości *RF* wyznaczonych dla analizowanych wzbogacalników stosowanych w procesach wzbogacania i odkamieniania węgla kamiennego (wąsy reprezentują rozrzut uzyskanych wyników)

was lower than in the feed coal. The *RF* value varied from 0.53 to 0.89 with the average of 0.69. A relatively low value of *RF* was obtained for the fine coal jigs as well (coal grain size 0.5–20 mm): from 0.85 to 1.45 with the average of 1.10. This may suggest difficulties in the separation of grains rich in mercury during these processes or the lack of such grains in feed coals.

For the flotation machines (coal grain size <0.5) the obtained results were not obvious. For individual cases very low or very high values of *RF* were observed. This can be explained by the different mode of mercury occurrence in the analyzed coals.

In Fig 4 a comparison of the *RF* values determined for the analyzed equipment items used in the hard coal washing and deshaling process was presented. In the light of the obtained results, it can be concluded, that mercury shows a tendency to occur in higher amounts in the rejects when compared to the feed coal both in the washing process (*RF* from 0.53 to 2.24 with the average of 1.15) and in the deshaling process (*RF* from 0.83 to 2.82 with the average of 1.50). This shows the possibility of the effective removal of mercury occurring in the adventitious inorganic constituents of the analyzed Polish hard coals. However, it should be noted, that the obtained results varied within a relatively high range, which should be explained by the difference in the mode of mercury occurrence in individual coals (Dziok et al. 2015, Zheng et al. 2008). This variability may cause low effectiveness of mercury removal for some coals. For such coals, the solution may be the thermal pretreatment of clean coals derived from the washing and deshaling processes at the temperatures of 200–300°C. This process allows for the removal of mercury occurring both in the organic matter as well as in the inorganic constituents characterized by a relatively low temperature of decomposition (Dziok & Strugała 2017). However it should be noted that the choice of an appropriate solution will depend on the investment and operating costs as well as on the quality requirements for hard coal including ash content and calorific value. When compared to the washing methods, the pneumatic vibrating FGX type separators are characterized by lower investment and operating costs (Baic et al. 2015).

Conclusions

The mercury content in the feed coals for coal cleaning varied from 54 to 218 μg/kg (the average of 106 μg/kg) and was smaller than the mercury content in the rejects separated from coal – from 55 to 319 µg/kg (the average of 125 µg/kg). The highest mercury content and the highest dispersion of results were recorded for the rejects derived from the dense media separators, as well as the pneumatic vibrating separators. The lowest values were obtained for the grain coal jigs.

In the light of the obtained results, it can be concluded that mercury shows a tendency to occur in higher amounts in the rejects when compared to the feed coal both in the washing process (*RF* from 0.53 to 2.24 with the average of 1.15) and in the deshaling process (*RF* from 0.83 to 2.82 with the average of 1.50), while the higher *RF* values were obtained for the dry deshaling process. This shows the possibility of effective mercury removal from the Polish hard coals. However, the choice of an appropriate solution will depend on the investment and operating costs as well as on the quality requirements for hard coal, including ash content and calorific value.

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Literatura – References

1. Baic I., Blaschke W. (2013). Analysis of the possibility of using air concentrating tables in order to obtain clean coal fuels and substitute natural aggregates. Polityka Energetyczna – Energy Policy Journal, 16(3), 247–260.
2. Baic I., Blaschke W., Szafarczyk J. (2014). The first FGX unit in the European Union', CPSI Journal a Magazine by the Cola Preparation Society of India., 16, 5-12.
3. Baic I., Blaschke W., Góralczyk S., Szaflarczyk J., Buchalik G. (2015). A New Method for Removing Organic Contaminants of Gangue from the Coal Output. Rocznik Ochrona Środowiska - Annual Set The Environment Protection, 17, 1274–1285.
4. Baic I., Blaschke W., Sobko W. (2015a) Badania nad odkamienianiem energetycznego węgla kamiennego na powietrznych stołach koncentracyjnych. Annual Set The Environment Protection, 17, 958-972.
5. Baic I., Blaschke W. (2017). Reduction of merkury content in steam coal – Preliminary study. 5th International Conference - Coal Washing: a sustainable approach towards greener environment CPSI Journal a Magazine by the Cola Preparation Society of India., 26, 141-151.
6. Baic I., Blaschke W. (2017a). Preliminary studies on the reduction of mercury content in steam coal through the use of air-vibrating concentration table. Rocznik Ochrona Środowiska - Annual Set The Environment Protection, 19, 480-496.
7. Baic I., Blaschke W. (2018). Preliminary Study on The Reduction of Mercury Content in Steam Coal by Using a Pneumatic Vibrating Concentrating Table. Inżynieria Mineralna - Journal of the Polish Mineral Engineering Society, 19(1), 141-149.
8. BAT-LCP (2017). Commission Implementing Decision (EU) 2017/1442 of 31 July 2017 establishing best available techniques (BAT) conclusions, under Directive 2010/75/EU of the European Parliament and of the Council, for large combustion plants.

9. Blaschke W., Szafarczyk J., Baic I., Sobko W. (2016). A Study of the Deshaling of Polish Hard Coal Using an FGX Unit Type of Air Concentrating Table. Proceedings of the 18th International Coal Preparation Congress. Saint Persburg. Russia. Vol. 2. 1143-1148. Ed. Springer
10. Dziok T., Strugała A., Rozwadowski A., Macherzyński M. (2015). Studies of the correlation between mercury content and the content of various forms of sulfur in Polish hard coals, Fuel, 159(1), 206–213.
11. Dziok T., Strugała A. (2017). Preliminary assessment of the possibility of mercury removal from hard coal with the use of air concentrating tables. Gospodarka Surowcami Mineralnymi – Mineral Resources Management, 33(4), 125–142.
12. Dziok T. (2018). A method of decreasing mercury content in bituminous coal. Przemysl Chemiczny, 97(1), 94–100.
13. Dziok T., Strugała A., Włodek A. (2019). Studies on mercury occurrence in inorganic constituents of Polish coking coals. Environmental Science and Pollution Research, 26(9), 8371–8382.
14. Ketris M.P., Yudovich Ya.E. (2009). Estimations of Clarkes for Carbonaceous biolithes: World averages for trace element contents in black shales and coals. International Journal of Coal Geology, 78, 135–148.
15. Li W.C., Tse H.F. (2015). Health risk and significance of mercury in the environment. Environmental Science and Pollution Research, 22, 192–201.
16. Pacyna J.M., Travnikov O., De Simone F., Hedgecock I.M., Sundseth K., Pacyna E.G., Steenhuisen F., Pirrone N., Munthe J., Kindbom K. (2016). Current and future levels of mercury atmospheric pollution on a global scale. Atmospheric Chemistry and Physics, 16, 12495–12511.
17. Wierońska F., Burmistrz P., Strugała A., Makowska D., Lech S. (2018). Effect of using coke dust as a sorbent for removing mercury from flue gases on the contents of selected ecotoxic elements in fly ash. Energy & Fuels, 32(5), 5693–5700.
18. Zheng L., Liu G., Qi C., Zhang Y., Wong M. (2008). The use of sequential extraction to determine the distribution and modes of occurrence of Mercury in Permian Huaibei coal, Anhui Province, China. International Journal of Coal Geology, 73, 139-155.

Badania skuteczności usuwania rtęci z węgla kamiennego w procesach przeróbki na mokro i na sucho

Emisja rtęci, z uwagi na jej toksyczne właściwości jest przedmiotem działań wielu legislacyjnych których przykładem jest m.in. przyjęcie w UE konkluzji BAT dla dużych obiektów energetycznego spalania. W przypadku dużych instalacji energetycznych znane i stosowane są różne metody usuwania rtęci ze spalin (etap post-combustion), natomiast w przypadku użytkowników domowych i instalacji energetycznych o małej mocy te metody nie są stosowane. Jest to spowodowane w głównej mierze wysokimi kosztami inwestycyjnymi. Najskuteczniejszym rozwiązaniem dla tej grupy użytkowników węgla jest usuwanie rtęci z węgla (etap pre-combustion), co umożliwi spalanie węgla o niskiej zawartości rtęci. Taki węgiel może być przygotowany w wyniku jego wzbogacania lub odkamieniania. Analizie poddano urządzenia do wzbogacania węgla kamiennego stosowane w polskim sektorze przeróbczym: płuczki zawiesinowe cieczy ciężkich, osadzarki miałowe i ziarnowe, flotowniki, a także separatory powietrzno-wibracyjne. Cztery pierwsze to urządzenia stosowane do wzbogacania węgla kamiennego na mokro, ostatnie to urządzenie do suchego odkamieniania urobku węglowego. Dla analizowanych urządzeń przebadano próbki nadaw kierowanych do wzbogacania oraz odpady. Dla oceny efektywności procesu wzbogacania wykorzystano wskaźnik RF, wyznaczony jako stosunek zawartości rtęci w odpadzie do nadawy kierowanej do wzbogacania. Uzyskane wartości RF wskazują na tendencję do pozostawania rtęci w odpadach zarówno w procesie wzbogacania na mokro (od 0,53 do 2,24 przy średniej 1,15) jak i suchego odkamieniania (od 0,83 do 2,82 przy średniej 1,50), przy czym wyższe wartości wskaźnika uzyskano dla suchego odkamieniania. Świadczy to o możliwości efektywnego usuwania rtęci z badanych polskich węgli kamiennych. Należy zaznaczyć, że uzyskane wyniki wahały się w dość szerokim zakresie, co należy tłumaczyć różnicami w formach występowania rtęci w poszczególnych węglach.

Słowa kluczowe: węgiel kamienny, wzbogacanie, odkamienianie, rtęć, usuwanie