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The leaching of mercury from hard coal and extractive waste in the acidic medium

Introduction

The studies on mercury content in hard coal and extractive waste are increasingly often encountered in the literature (e.g. Michalska and Białecka 2012; Dziok et al. 2015; Kosa and Kicińska 2016; Klojzy-Karczmarczyk and Mazurek 2013, 2019; Białecka and Pyka, ed. 2016; Wichliński et al. 2016). The knowledge of leachable forms amount in the total content of this element becomes especially important. It is significant in the case of considerations related to the coal and by-products use in various sectors of the economy. This is also important in the case of looking for new or modifying the existing methods for various extractive waste types management or disposal. The percentage of leachable forms in the total element's content definitely affects possibilities of pollutants migration to the surrounding environment. The mercury in coals and in extractive waste may be related both to the organic and mineral matter (e.g. Bojakowska and Sokołowska 2001; Diehl et al. 2004; Dai et al. 2006; Głodek and Pacyna 2007; Bielowicz and Misiak 2016). The leachability of

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mercury from the analyzed material depends mainly on the forms of this element existence (O'Connor et al. 2019). In addition, there is a number of factors in the environment, which affect the process of mercury leaching from various compounds. These are mainly the refinement and the shape of material grains, the temperature of the environment, the ratio of the liquid to solid phase (L/S – *liquid/solid*), the redox potential, pH conditions of the environment, and the time of studied material contact with rainwater (e.g. Król 2011; Vitková et al. 2009; Witczak and Adamczyk 1995).

The content of mercury in various environmental samples and in waste is clearly diversified and depends on many factors. The percentage of the leachable form in its total content, calculated based on the amount of element leaching in assumed environmental conditions, is referred to in the literature as the level of leaching (Mizerna and Król 2015). The previous laboratory studies of the authors, with the use of deionized water as the leaching medium, show that mercury from samples of superficial soils, deposits, or extractive waste is released to the solution, at amounts from approx. 1 to 20% of its total content in the sample (Klojzy-Karczmarczyk and Mazurek 2005, 2015, 2017, 2019). An mean level of mercury leaching for environmental samples of various origins is around a few percent. In particular, based on the carried out analyses and studies, it is possible to state that an mean level of leaching for hard coals and extractive waste of the coal mining sector is approx. 3–4%, but it can reach nearly 8% (Klojzy-Karczmarczyk and Mazurek 2019). It is possible to state that under favorable conditions mercury may transfer to the solution and migrate as the pollution in the environment (e.g. Macioszczyk and Dobrzyński 2002; Boszke et al. 2003). However, on the other hand, the migration of released mercury compounds may be stopped due to a high delay coefficient R (Klojzy-Karczmarczyk 2016).

The amount of results on mercury leaching from environmental samples, and hence the amount of studies on the determination of the mercury leaching level, is still insufficient. The studies presented in this paper were aimed at determination of the total mercury content and its leachable form in hard coals and by-products of coal mining, that is in aggregate or extractive waste, like barren rock or hard coal sludge, referred to in the following part in the paper as coal sludge. The studies were carried out in laboratory conditions, with the use of various leaching solutions, simulating different environmental conditions. In the literature one can find studies on mercury leaching from coal and extractive waste with the use of deionized water, but there are no studies on this element leaching in an acidified medium. The paper presents the studies on mercury leaching under conditions simulating a neutral environment and an acidic environment, applying an appropriate research methodology, as well as the results of the studies.

1. Description of samples

Six samples of hard coal and 10 samples of by-products of hard coal mining, referred to overall as extractive waste, were designed for the analysis of total mercury content and of the amount of its leaching from the material. The samples for studies originated from the same sampling series as in the previous studies (Klojzy-Karczmarczyk and Mazurek 2019). The analyzed samples come from the USCB (Upper Silesian Coal Basin). They were selected randomly from a larger batch of material and they are not related of genetic origin. The results of petrographic or mineralogical studies of such samples are varied. These can be found in other published materials (e.g. Szlugaj 2020). The objective consisted in showing the relationship between the level of mercury leaching and the type of samples and pH conditions of the environment, as well as in showing a difference in the obtained results for extractive waste compared to hard coal. The following were designed for leachability studies (in mg/dm^3 of the solution), and hence leaching (in mg/kg DM of the material):

1. Hard coal samples from selected USCB seams; the year of sampling – 2011, 6 random selected samples were analyzed (Table 2: hard coal 1–6).
2. Extractive waste from the hard coal mining sector, directly from the production; overall 10 samples were analyzed (Table 2 and Table 3: aggregate 1–3 and coal sludge 1–4):
   - aggregate (barren rock): 3 samples were prepared, several fractions were separated, two grain fractions < 6 mm (the finest fraction) and 80–120 mm (the thicknes fraction) were selected for testing (a total of 6 samples were analyzed); the aggregate is frequently used as a raw material and it is not treated as waste (Galos and Szlugaj 2014; Szlugaj 2020),
   - hard coal sludge (4 samples were analyzed), referred to as coal sludge.

2. Applied methodology of analysis

A number of testing methods may be used in the laboratory practice, allowing to determine the amount of leachability in the solution (in mg/dm^3), and the next leaching from solid samples (in mg/kg DM). In effect, such results provide the basis to determine the level of leaching (release) of mercury, but also of other metals (in%). The amount of mercury release to a large extent depends on the applied methodology (e.g. Makowska et al. 2018; Mizerna and Król 2015; Rosik-Dulewska and Karwaczyńska 2008). The selection of an appropriate method for leachability studying is a significant element of the environmental hazard assessment. The paper presents laboratory studies carried out under static conditions with the involvement of different leaching mediums. The studies presented here allow to observe the effects of mercury compounds solubility depending on the environment's pH.

Classical leachability tests under static conditions, most frequently applied in the laboratory work, use deionized water as the leaching medium. This allows to determine the amount of individual pollutants leaching in a neutral environment. In fact, on spoil heaps of Carboniferous waste the pH of porous solutions shows significant dynamics of changes within a wide range of pH, from neutral to definitely acidic. Over time, weathering and oxidisation of pyrite proceed. At simultaneous lack of buffering compounds the environment becomes acidified and pH values of porous solutions decrease to low values, even to 2.5–3 (e.g. Szczepańska and Twardowska 1999; Klojzy-Karczmarczyk 2003; Gawor et. al. 2014; Probierz et al. 2017). Such conditions are favorable for heavy metals release. The paper presents static leachability tests carried out in the neutral medium and acidic medium. The pH values of the leaching solution were reduced from 7 to approx. 3 (Tables 2–4). Laboratory studies on mercury leachability were carried out in accordance with procedures specified in the appropriate methodology:

- leachability under conditions close to neutral (deionized water – the leaching medium, test 1:10), leaching was carried out in accordance with principles of standard PN EN 12457/1-4 *Characterisation of waste – Leaching – Compliance test for leaching of granular waste materials and sludges*; conditions correspond to initial stages of Carboniferous rock waste deposition;
- leachability under acidic conditions (solution acidified with acetic acid was the leaching medium, test 1:20), the leaching was carried out in accordance with principles of the TCLP (*Toxicity Characteristic Leaching Procedure*) method; conditions correspond to deposition of Carboniferous rock waste after many years of the facility operation.

The assumptions of each applied method were adapted to the research equipment of the MEERI PAS laboratory, where the studies were carried out. The extraction was carried out in one stage. Table 1 provides the list of basic principles used in the research process.

Table 1. Parameters of the methodology applied to study the mercury leachability from hard coals and extractive waste

Tabela 1. Parametry zastosowanej metodyki badania wymywalności rtęci z węgli i odpadów wydobywczych

Parameter	Leaching in a neutral medium (static test)	Leaching in an acidic medium (static test)
Basic assumptions	PN-EN 12457/1-4 method	TCLP method
Sample weight	90 g	100 g
Material’s particle size	<10 mm	<9.5 mm
L/S (liquid/solid) ratio	10/1 (1:10 test)	20/1 (1:20 test)
Leaching liquid	Deionized water pH 7	Acetic acid solution pH approx. 3
Shaking method	Laboratory shaker	Laboratory shaker
Shaking time	24 h ± 0.5	18 h ± 2
Type of filter	Membrane filter Pores Ø 0.45 µm	Membrane filter Pores Ø 0.45 µm
Determination of Hg content	Atomic absorption spectrometer AMA 254	Atomic absorption spectrometer AMA 254

Methodology adapted to the research equipment of MEERI PAS laboratory.

The leaching with acid medium was carried out using the acetic acid solution. The concentrated acetic acid of 80% pure was used with deionized water. The solution has been diluted with deionized water until the pH was about 3.

An Altec atomic absorption spectrometer AMA 254 was used to determine the mercury content. The applied analytical method provides the result of mercury determination as a sum of all Hg forms existing in the sample. High-temperature mineralization and the application of an appropriate catalyst allows good results for the majority of mercury speciations, coexisting in environmental samples, to be achieved. The total mercury content in the samples was determined for the air-dry state and the obtained results recalculated to the dry state and provided in mg/kg DM. The moisture content of the analyzed hard coal samples was around 1.5–2.3%, while for extractive waste around 0.9–2.1%. The drying was carried out till a constant weight was achieved (approx. 4–5 h). The results of analytical determinations for the eluate, provided in mg/dm^3, were converted into the released amount of the pollutant in relation to the dry mass of the sample and also provided in mg/kg DM. The obtained results are specified in Tables 2–4 and in Figures 1 and 2. The two determinations of mercury content were made and the arithmetic mean was given for each case. The arithmetic mean and standard deviation from double data was calculated using Excel software. The Limit of Quantification (LOQ) for Hg analysis in solid samples is 0.0005 mg/kg. The LOQ value for Hg analysis in liquid samples is 0.0005 mg/dm^3.

3. Results and discussion

The application of two different research methods allows to simulate different environmental conditions. The total mercury content and the amount of leaching mercury form from solid samples were determined for all selected samples. It was based on tests of the mercury leachability and its content in the solution. In addition, the percentage of leachable form in the total element content was calculated, that is the level of mercury release from the material (level of leaching) (Table 5 and 6). The observed characteristic of leaching process differs for samples of hard coals and of extractive waste. The obtained values confirm the conclusions from the previous studies (Klojzy-Karczmarczyk and Mazurek 2019).

3.1. Hard coal

The presented paper analyses the results of studies for 6 samples of hard coals, randomly selected from seams of the Upper-Silesian Coal Basin. For the chosen material the total mercury content ranged from 0.0384 mg/kg to 0.1049 mg/kg (Table 2). In the 2013 paper (Klojzy-Karczmarczyk and Mazurek 2013) the results published for 100 samples from the same area show the total mercury content between 0.0029 and 0.3026 mg/kg, at its mean value of approx. 0.0739 mg/kg. The amount of mercury leaching from coal samples varies and depends on the applied leaching medium. In the process of leaching with deionized water (in accordance with the PN-EN 12457/2 method) the amount of mercury leaching ranges from 0.0010 mg/kg to 0.0040 mg/kg. The percentage of leachable form in the total content is around 1.24–3.81%. The obtained results are comparable with those obtained by the authors in the 2019 paper. In the process of leaching under acidic conditions (in accordance with principles described in the TCLP method) the leaching of mercury from hard coals increases. The amount of mercury leaching (under conditions of the environment's pH of approx. 3) ranges between 0.0019 mg/kg and 0.0055 mg/kg. The percentage of the leachable form grows to values from 2.49 to 5.24%.

Table 2. Mercury leaching from hard coal samples depending on the pH medium

Tabela 2. Wymywanie rtęci z próbek węgla kamiennego w zależności od pH środowiska

The hard coal samples from selected seams of the USCB					
No of sample	Hgd total content* (mg/kg DM)	Leaching of Hg (1:10 test – deionized water)		Leaching of Hg (1:20 test – acidic medium)	
		pH of solution**	Leaching (mg/kg DM)	pH of solution**	Leaching (mg/kg DM)
Hard coal 1	0.0764	7.82	0.0010	3.21	0.0019
Hard coal 2	0.1049	7.80	0.0040	3.19	0.0055
Hard coal 3	0.0600	7.68	0.0012	3.22	0.0021
Hard coal 4	0.0881	7.57	0.0026	3.22	0.0030
Hard coal 5	0.0384	7.78	0.0013	3.18	0.0020
Hard coal 6	0.0535	7.46	0.0014	3.15	0.0025

* Total content Hg in dry mass.
** pH of the solution measured after shaking.

3.2. Extractive waste

Aggregate (barren rock as a by-product, raw material, Table 3) and coal sludge (Table 4) were studied and analyzed in the group of extractive waste. Clear diversification of the leachable fraction percentage is observed in individual groups of the studied material, that is of the level of leaching depending on the nature of the leaching medium (Figures 1 and 2).

The extractive waste of aggregate type features a higher total mercury content in the finest fraction <6 mm, from 0.2071 to 0.4564 mg/kg, and a definitely lower content in the fraction 80–120 mm, from 0.0485 to 0.1006 mg/kg. The amount of leaching in deionized

Table 3. Mercury leaching from aggregate (barren rock) samples depending on the pH medium

Tabela 3. Wymywanie rtęci z próbek kruszyw (skała płonna) w zależności od pH środowiska

The aggregate (barren rock) from hard coal mining – extractive waste					
No of sample	Hg^d total content* (mg/kg DM)	Leaching of Hg (1:10 test – deionized water)		Leaching of Hg (1:20 test – acidic medium)	
		pH of solution**	Leaching (mg/kg DM)	pH of solution**	Leaching (mg/kg DM)
Aggregate 1 fraction <6 mm	0.2777	7.42	0.0030	3.11	0.0029
Aggregate 1 fraction 80–120 mm	0.0867	7.42	0.0015	3.11	0.0023
Aggregate 2 fraction <6 mm	0.2071	7.42	0.0031	3.30	0.0032
Aggregate 2 fraction 80–120 mm	0.0485	7.53	0.0013	3.38	0.0020
Aggregate 3 fraction <6 mm	0.4564	7.50	0.0070	2.95	0.0114
Aggregate 3 fraction 80–120 mm	0.1006	7.50	0.0022	2.90	0.0028

* Total content Hg in dry mass.
** pH of the solution measured after shaking.

water is comparable for both fractions and is around 0.0013−0.0070 mg/kg. The percentage of leachable form in the finest fraction is slightly lower than in the 80–120 mm fraction. The level of leaching in the grain fraction <6 mm ranges from 1.08 to 1.53%, while in the 80–120 mm fraction this level is from 1.73 to 2.58%. In the acidic environment the amount of leaching was observed to grow to 0.0020–0.0028 mg/kg for the 80–120 mm fraction. For the fine fraction with particle size <6 mm no increase in the leachability in the acidic environment was observed for two samples. An increase in leachability has been observed only for one sample, which obviously affects the mean value of measurements in this waste group (Figure 1).

Coal sludge features the total mercury content of 0.1368−0.2178 mg/kg. Low values of leaching are observed in deionized water – around 0.0018−0.0055 mg/kg. During mercury leaching in the acidic environment the leachability goes up to 0.0038−0.0081 mg/kg. The percentage of leachable form is comparable with values obtained for aggregate and amounts from 0.88 to 2.53% for leaching in a neutral environment and from 1.95 to 3.95% for leaching in the acidic environment.

The total mercury content in tested extractive waste is comparable with results provided in the literature both for aggregate and for sludge. It should be emphasized that

Table 4. Mercury leaching from coal sludge samples depending on the pH medium

Tabela 4. Wymywanie rtęci z próbek mułów węgla kamiennego w zależności od pH środowiska

The hard coal sludge samples (after dewatering filters) – extractive waste					
No of sample	Hg^d total content* (mg/kg DM)	Leaching of Hg (1:10 test – deionized water)		Leaching of Hg (1:20 test – acidic medium)	
		pH of solution**	Leaching (mg/kg DM)	pH of solution**	Leaching (mg/kg DM)
Coal sludge 1	0.1950	7.69	0.0025	2.98	0.0038
Coal sludge 2	0.2039	7.55	0.0018	2.92	0.0045
Coal sludge 3	0.1368	7.55	0.0034	3.25	0.0054
Coal sludge 4	0.2178	7.60	0.0055	2.99	0.0081

* Total content Hg in dry mass.
** pH of the solution measured after shaking.

the number of publications in this field is small. The total mercury content in the waste from coal mining and preparation according to the literature data is within a range of 0.006–0.380 mg/kg (Michalska and Białecka 2012; Dziok et al. 2015; Klojzy-Karczmarczyk 2016). The total mercury content in coal sludge is around 0.015–0.229 mg/kg (Wichliński et al. 2016; Białecka and Pyka, eds. 2016). Similar to hard coal, in the available literature there are no results on studies of mercury leaching from the extractive waste, collected from the production line. Instead, it is possible to find previous papers of the authors, presenting the equally low leachability of this element from a similar material with the use of deionized water as the leaching medium (Klojzy-Karczmarczyk et al. 2016; Klojzy-Karczmarczyk and Mazurek 2019).

3.3. Mercury content comparison

Taking the total mercury content into consideration, both hard coal and extractive waste and parameter values obtained for them do not exceed standards established for neutral extractive waste in accordance with the Regulation of the Minister of Environment *on classification criteria for extractive waste as neutral waste* (Dz.U. of 2011 No 175, item 1048). For comparison, the total mercury content of the waste of other groups is varied. The mercury content in landfilled foundry wastes, which consist mainly of spent foundry sands (SFS), is usually low (mean 0,030 mg/kg DM) (Bożym and Klojzy-Karczmarczyk 2021). On the other hand, in foundry dusts the mercury content may be higher (to 0.130 mg/kg DM), especially in dust from electric furnaces (Electric Arc Furnane Dust, EAFD), even above 4 mg/kg DM (Bożym and Klojzy-Karczmarczyk 2020).

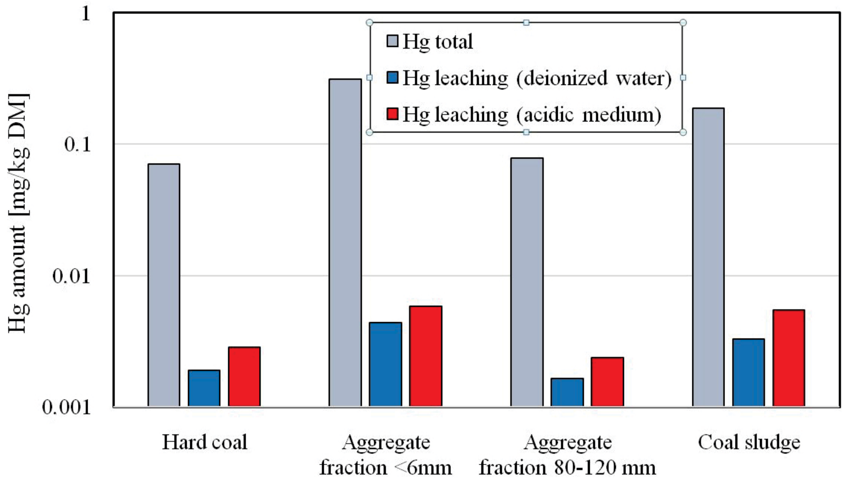

Fig. 1. The leaching of Hg (deionized water or acidic medium) compared to the total Hg content of the tested samples

Rys. 1. Wielkość wymywania Hg (woda dejonizowana lub środowisko kwaśne) w porównaniu z całkowitą zawartością Hg w badanych próbkach

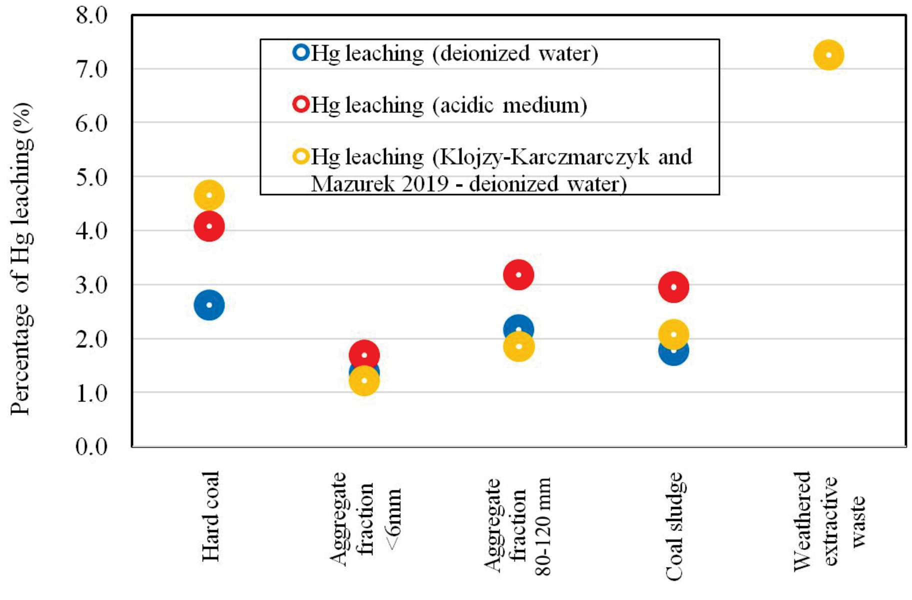

Fig. 2. The comparison of the level of Hg leaching (deionized water or acidic medium) from the tested materials. The results from previous studies are attached to the chart

Rys. 2. Porównanie stopnia wymywania Hg (woda dejonizowana lub środowisko kwaśne) dla badanych materiałów. Do wykresu włączono wyniki z wcześniejszych badań

When analyzing the amount of mercury leaching, the studied material in the form of hard coal and extractive waste, i.e. aggregate and coal sludge, meets the criteria set to neutral waste allowed for landfilling in a neutral waste landfill in accordance with the Regulation of the Minister of Economy dated 16 July 2015 *on allowing the waste to be landfilled in landfills* (Dz.U. of 2015, item 1277).

In general, the studied material shows diversification of the total mercury content and of its leachable fraction. An increase in mercury leachability is observed in the acidic medium for each group of the studied materials (Figures 1 and 2). The highest percentage of the

Table 5. The percentage of mercury leaching in the total content for various types of samples analyzed with deionized water medium

Tabela 5. Udział formy wymywalnej Hg w całkowitej zawartości z podziałem na poszczególne rodzaje analizowanego materiału w środowisku obojętnym

Type of samples		Number of samples	The percentage of Hg leaching (%) 1:10 test with deionized water (pH 7.42–7.82)		
			min. value	max. value	arithmetic mean
Hard coal samples from selected seams of the USCB		6	1.24	3.81	2.63
Extractive waste from hard coal mining	Aggregate fraction <6 mm	3	1.08	1.53	1.37
	Aggregate 80–120 mm	3	1.73	2.58	2.17
	Coal sludges	4	0.88	2.53	1.79
Extractive waste total		10			1.78

Table 6. The percentage of mercury leaching in the total content for various types of samples analyzed with acidic medium

Tabela 6. Udział formy wymywalnej Hg w całkowitej zawartości z podziałem na poszczególne rodzaje analizowanego materiału w środowisku kwaśnym

Type of samples		Number of samples	The percentage of Hg leaching (%) 1:20 test with acidic medium (pH 2.90–3.38)		
			min. value	max. value	arithmetic mean
Hard coal samples from selected seams of the USCB		6	2.49	5.24	4.09
Extractive waste from hard coal mining	Aggregate fraction <6 mm	3	1.04	2.50	1.70
	Aggregate 80–120 mm	3	2.65	4.12	3.19
	Coal sludges	4	1.95	3.95	2.96
Extractive waste total		10			2.62

leachable form in the total mercury content is observed for hard coal samples. For the same samples the highest increase is observed in mercury leachability in the acidic medium. For extractive waste samples both values are slightly lower. The obtained results may suggest that the statement, that mercury compounds in aggregate (fresh waste) and in coal sludge, which are most likely largely insoluble mercury sulphides, is right. Instead, hard coals mercury is probably largely bound in organic compounds featuring higher solubility than sulphides. Taking the leachability in deionized water of weathered extractive waste into account (Figure 2), after many years of storage in the spoil heap, a clear increase is observed, a several-fold increase in leachability as compared with fresh waste, which results from sulphur compounds conversion towards well soluble sulphates. This studies confirmed by mercury speciation analysis carried out for soils and dusts according to O'Connor et al. (O'Connor et al. 2019).

Due to lack of similar studies for coal waste in the literature, in particular on leachability in the acidic environment, it is not possible to compare the obtained results with other authors. Mainly the reports of acid leaching of Hg concern soil or dust (Coufalík et al. 2012; O'Connor et al. 2019). However, there are reports on leaching other metals under various pH conditions of the environment, with the use of a similar methodology. In the paper by D. Makowska et al. (Makowska et al. 2018) the highest concentration of the studied arsenic was recorded just in the extract prepared in accordance with the TCLP method, using a solution of acetic acid with pH = 3, as compared with a water extract and a classical leaching test. In the paper by D.B. Sarode et al. (Sarode et al. 2010), during studies on leaching of various heavy metals, such as Zn, Ni, Cu, Fe, Pb, Mn, and Mg from the fly ash and their admixtures, a higher leachability was also found with the use of the TCLP method as compared with classical water extracts with the use of deionized water. No increase in leachability was observed for Cd at the application of the TCLP method. Other published paper also indicate an increase in leaching of toxic elements in water solutions with increasing acidity (e.g Bożym 2017; Kicińska 2020; Król et al. 2020).

Conclusions

The paper presents the results of studies on the total mercury content and on the amount of mercury leaching from samples of hard coal and of by-products of this raw material preparation, like aggregate (barren rock) or coal sludge. The leaching was carried out reducing the pH of the environment from approx. 7 to 3. The selection of an appropriate method for leachability studying is a significant element in the assessment of the environmental hazard. The paper presents laboratory studies carried out under static conditions with the involvement of different leaching mediums. Laboratory studies on mercury leachability were carried out in accordance with procedures specified in the appropriate methodology (based on PN EN 12457/1-4 and TCLP methods).

The percentage of leachable form in the total content of this element, that is the level of mercury released from the material (level of leaching) versus pH, was determined based on the total content and the amount of leaching (Figure 2). Tables 5 and 6 present the percentage of leachable form in individual groups of samples. In hard coals taken from the USCB, the level of leaching was 2.6% on mean. Under acidic environmental conditions the amount of leaching increases by approx. 1.5–2 times, to an mean value of 4.1%. The extractive waste features high variability of the leachable mercury form. By-products of hard coal production, like aggregate (barren rock managed mainly as a raw material), show the percentage of leachable mercury form on an mean level of 1.4–2.2%, depending on the material's fraction. With pH of the leaching medium decreasing to approx. 3, the amount of leaching grows by a maximum of 1.6 times, to mean values of 1.7–3.2%. It should be noticed that higher values of the leachable fraction are found for a coarser material. In extractive waste, such as hard coal sludge, an mean percentage of mercury leachable forms is approx. 1.8%. Under acidified conditions the percentage of leachable form increases in the eluate by 1.5–2.5 times and reaches an mean value of 3.0%.

The characteristic of leaching is diversified for various groups of the studied material, different for coals and for individual types of the waste material. Based on the carried out analysis it is possible to draw conclusions about factors, which affect the mercury content in various forms and the amount of this element leaching in the environment. The performed leachability tests have shown increased mercury leachability at the reduction of the environment's pH to a value of approx. 3. In general, the leachability of mercury from hard coals and extractive waste is low, and the leachability in an acidic environment grows approx. two-fold. Hence such factors as the type and origin of samples, their grain composition, and additionally the pH conditions of leaching, shown in the paper, have basic importance for the process of mercury leaching from the material. However, the time of material seasoning and its weathering processes have the greatest impact on increasing the leachability of mercury from the waste material from the hard coal mining sector, and the leachability in weathered materials increases 3–6 times. The time of seasoning is especially important for extractive waste, which was presented in the previous studies (Klojzy-Karczmarczyk and Mazurek 2019) and in Figure 2.

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THE LEACHING OF MERCURY FROM HARD COAL AND EXTRACTIVE WASTE IN THE ACIDIC MEDIUM

Keywords

leaching, hard coal, total content, extractive waste, Mercury

Abstract

Sixteen samples were designed for analysis (hard coal, aggregate – barren rock, hard coal sludge). The total mercury content and the amount of mercury leaching were determined. The percentage of leachable form in the total content was calculated. The studies were carried out under various pH medium. The leachability under conditions close to neutral was determined in accordance with the PN EN 12457/1-4 standard. The leachability under acidic medium (pH of the solution – approx. 3) was determined in accordance with principles of the TCLP method. The mercury content was determined by means of the AAS method. For hard coal the total mercury content was 0.0384–0.1049 mg/kg. The level of leaching on mean was 2.6%. At the acidic medium the amount of leaching increases to an mean 4.1%. The extractive waste of aggregate type features a higher total mercury content in the finest fraction < 6 mm (up to 0.4564 mg/kg) and a lower content in the fraction 80–120 mm (up to 0.1006 mg/kg). The aggregate shows the percentage of the leachable form on mean from 1.4 to 2.2%. With pH decreasing to approx. 3, the amount of leaching grows up to mean values of 1.7–3.2%. Coal sludge features the total mercury content of 0.1368–0.2178 mg/kg. The percentage of mercury leachable form is approx. 1.8%. With pH decreasing the value increases to mean value of 3.0%. In general, the leachability of mercury from hard coals and extractive waste is low, and the leachability in an acidic medium grows approx. twice. Such factors as the type and origin of samples, their grain composition, and the pH conditions, have basic importance for the process. The time of waste seasoning and its weathering processes have the greatest impact on increasing the leaching of mercury from the extractive waste.

WYMYWANIE RTĘCI Z WĘGLI KAMIENNYCH I ODPADÓW WYDOBYWCZYCH W ŚRODOWISKU KWAŚNYM

Słowa kluczowe

odpady wydobywcze, węgiel kamienny, zawartość całkowita, wymywanie, rtęć

Streszczenie

Do analizy przeznaczono 16 próbek (węgiel kamienny, kruszywa – skała płonna, muły węgla kamiennego). Określono zawartość całkowitą rtęci oraz wielkość wymywania. Obliczono ponadto udział formy wymywalnej w całkowitej zawartości pierwiastka. Badania prowadzono w różnych warunkach pH środowiska. Wymywalność w warunkach obojętnych wykonano zgodnie z wytycznymi normy PN EN 12457/1-4. Wymywalność w warunkach kwaśnych (pH roztworu około 3) wykonano w oparciu o metodę TCLP. Przy oznaczaniu zawartości rtęci wykorzystano metodę AAS. Dla węgla kamiennego zawartość rtęci całkowitej kształtuje się w granicach 0,0384–0,1049 mg/kg. Wielkość wymycia kształtuje się na średnim poziomie 2,6%. W kwaśnym środowisku wielkość wymywania zwiększa się do średniej wartości 4,1%. Odpady wydobywcze typu kruszywa charakteryzują się wyższą zawartością rtęci całkowitej we frakcji najdrobniejszej < 6 mm (do 0,4564 mg/kg) i niższą we frakcji 80–120 mm (do 0,1006 mg/kg). Udział formy wymywalnej rtęci w kruszywach jest na średnim poziomie 1,4–2,2%. Przy obniżaniu pH do około 3, wielkość wymywania zwiększa się do średnich wartości 1,7–3,2%. Muły węglowe charakteryzują się zawartością rtęci całkowitej na poziomie 0,1368–0,2178 mg/kg. Średni udział formy wymywalnej jest na poziomie 1,8%. Przy obniżaniu pH udział ten osiąga średnią wartość 3,0%. Ogólnie wymywalność rtęci z węgli kamiennych oraz odpadów wydobywczych jest niska, a zwiększenie wymywalności w środowisku kwaśnym jest około dwukrotne. Podstawowe znaczenie dla procesu wymywania mają rodzaj i pochodzenie próbek, ich skład granulometryczny oraz warunki pH. Największy wpływ na zwiększenie wymywalności rtęci z materiału odpadowego sektora wydobywczego węgla kamiennego mają czas sezonowania materiału i procesy wietrzeniowe.