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Comparative analysis of the evaluation of the influence of waste on the environment depending on the applied research method (on the example of brown coal ash)

Introduction

In Poland the production of electrical energy is 70% based on thermal fossil fuels processing, mainly of bituminous and brown coal. A constantly growing need for energy is strictly connected with the generation of larger and larger amounts of energetic wastes.

Due to the abundant resources of brown coal in Poland, it is one of the most important power raw materials. The documented geological brown coal resources are over 26 million tons, while the possibility of its occurrence on the carboniferous areas is assessed to be over 140 billion tons. The fact points at the high potential of the fuel's energetic ex-

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plotation. Nowadays, it is applied on a wide scale in professional energy, which has been experiencing an entire range of transformations in recent years (Rosik-Dulewska et al. 2016).

The generation of fly ash in Poland achieved the value of 3.258 m.tons/year in 2016, 3.414 m.tons/year (Statistical Year Environment Protection Central Statistical Office 2017 and 2018), which constituted 4.18%, as well as 3.0% in the annual, general balance of the wastes produced (exclusive of municipal garbage). Great amount of generated ashes contain huge heavy metals which could be toxic for plants and animals after being released into environment. Lots of researchers have investigated the leaching behavior of heavy metals in fly ash using sequential extraction procedures, also in the case of “new types” – biomass ashes (Jukić et al. 2017; Zhao et al. 2018). Very toxic metals (Cd, Pb) could be present only in not-mobile fractions in coal ashes, however their potential toxicity is close to zero (Krgović et al. 2014). The selection of the right method of using energy waste use requires a very precise knowledge of their physical properties as well as their chemical and mineralogical composition (Koniecznyński et al. 2017). Becoming familiar with the characteristics of the wastes allows for their relegation to an appropriate type as well as an assessment to what kinds of goods they can be used for, in order to fulfil all the requirements they are attached with. Due to the knowledge of the waste properties, the choice of an appropriate processing technology for them is possible as well.

Specific physical, chemical and mineralogical properties as well as the massive generation of fly ash allows for their wide range of use as raw materials in many economic fields, including building construction, pottery, road construction and in the aviation as well. Today, over 55% of the fly ash produced in Poland plays a meaningful role in the building materials industry (Rosik-Dulewska et al. 2016).

1. Materials and methods

The fly ash produced as a result of brown coal burning was submitted for research, the aim of which was to compare the assessment most frequently carried out in respect of the influence of wastes on the environment through leaching tests (PN-G-04502:2014-11) for research conducted with the use of sequential chemical extraction (the BCR method was suggested in the research).

Three-stage leaching test (according to PN-EN 12457:2006) was carried out with a constant proportion of the waste dry mass to the distilled water 1:10. After weighing a sample and pouring distilled water over it, it was shaken for about 4 hours, then was left for 16 hours in static conditions. After the time it was shaken again for 4 hours and left for 2 hours in order to perform sedimentation of the solid parts. The supernatant received was infiltrated through a filter made of soft tissue paper. Distilled water was again poured over the remaining sediment (of the volume equal to the decanted liquid) and the aforementioned procedure was repeated two more times.

A dozen of important indications have been made in water extracts, nevertheless, in this paper only the ones presented below are shown:

- ◆ The reaction conducted by the electrometric method, in accordance with PN-C-45300-03:1985.
- ◆ The electrolytic conductance in accordance with PN-EN 27888:1999.

The contents of six trace elements (Ni, Zn, Cd, Cu, Cr, Pb) as well as three macroelements (Li, Na, K) was noted. The trace elements were determined by the ASA method, with the use of the ICE 3000 Thermo Scientific spectrometer, while the macroelements with the use of BWB-XP flame photometer.

Loads of lixiviated pollutants has been counted from every level of eluting (q_1 , q_2 , q_3) as well as their sum (Q), on the basis of the formulas in the PN-EN 12457:2006 standard. In the ashes, on the other hand, a qualitative analysis of seven trace elements (Cu, Zn, Cd, Ni, Pb, Cr) has been conducted and of three macroelements (Li, Na, K) with the help of chemical extraction developed and advised in the European Union countries by the Communities Bureau of References – BCR (Wang et al. 2019).

As a result, a distribution of the indicated metals contents was achieved in four different types of connections with the solid substance:

- ◆ fraction I – renewable metals and attached with carbonates (the most easily available metals for the environment),
- ◆ fraction II – oxide or reducible fraction (metals attached with hydrated oxide of iron and manganese),
- ◆ fraction III – organic fraction, oxidized (metals attached with organic matter and sulphides),
- ◆ fraction IV – residual fraction (metals attached with mineral deposit).

The procedure of indicating the particular fractions was carried out in the following way:

- ◆ *fraction I* – 20 cm³ 0.11 M of acetic acid was added to the sample weights, then they were shaken at room temperature and finally the samples were spun.
- ◆ *fraction II* – 25 cm³ 0.5 M of Hydroxylammonium chloride was added to the fraction I deposit that was achieved as a result of the spinning process (the pH was kept in the range: 2–3), next it was shaken for 16 hours at room temperature and spun afterwards.
- ◆ *fraction III* – 10 cm³ 30% of peroxide was added to the fraction II spinning deposits and then left at room temperature for 1 hour, the pH was kept in the range: 2–3). Next, the tests were heated up and kept at the temperature of about 85°C for 1.5 h, subsequently 10 ml of 30% peroxide was added again and the process of heating up was continued for another 24 hours. After the mixture was chilled, 40 cm³ 1 M of ammonium acetate was added and was shaken for 16 hours at room temperature and spun afterwards.
- ◆ *fraction IV* – 10 cm³ of aqua regia was added to the fraction III spinning deposit and left at room temperature for 24 hours, next another 10 cm³ of aqua regia was added and was heated up to the temperature of about 85°C for 2 h. It was then chilled and spun.

The content of metals in all the received eluates was also indicated by the use of atomic absorption spectroscopy (ASA) on the ICE 3000 Thermo Scientific atomic absorption spectrometer.

2. Results and discussion

2.1. The content of trace elements – leaching tests

The process of lixiviation of soluble components was carried out in static conditions with the proportion solid phase (S): solution (L) = 1:10 in the contact time 26 h, while intensive stirring took 8 h and the resting time of the suspension – 18 h.

The research results of physicochemical parameters were written in Table 1 and compared with the limit values that are in the Regulation of the Minister of Maritime Economy and Inland Navigation of July 12, 2019 on Substances Particularly Harmful to the Aquatic Environment and Conditions to be Met when Introducing Sewage into Waters or into the

Table 1. The comparison of research of the analytical water essences from the three-stage leaching test from fly ash produced from brown coal in mg/dm³ with the values presented in the Regulation of the Minister of Maritime Economy and Inland Navigation of July 12, 2019

Tabela 1. Porównanie wyników badań analitycznych wyciągów wodnych z trójstopniowego testu wymywalności z popiołu lotnego z węgla brunatnego w mg/dm³ z wartościami zamieszczonymi w Rozporządzeniu Ministra Gospodarki Morskiej i Żeglugi Śródlądowej z dnia 12 lipca 2019 r.

Parameter	1°	2°	3°	<i>Minister of Maritime Economy and Inland Navigation</i> Limit values 12 July 2019
pH	12.3	11.9	11.8	6.5–9
μS/cm	9 010	2950	1630	–
Ni mg/dm ³	0.040	0.040	0.040	0.5
Zn mg/dm ³	0.010	0.025	0.003	2
Cd mg/dm ³	0.030	0.030	0.030	0.05
Cu mg/dm ³	0.013	0.017	0.014	0.5
Cr mg/dm ³	0.041	0.043	0.030	0.1
Pb mg/dm ³	0.190	0.196	0.190	0.5
Li mg/dm ³	0.70	0.70	0.80	–
Na mg/dm ³	73.80	72.00	81.20	800
K mg/dm ³	33.10	32.70	36.50	80

Ground, as well as when Discharging Rainwater or Snowmelt into Waters or into Equipment Water (Journal of Laws 2019, item 1311).

The reaction of the solutions received was alkalic and pH was decreasing along with the lixiviation factor from 12.3 (eluate from the first leaching stage), through 11.9 (eluate from the second leaching stage). Each from the values received exceeded the range of the limit value (6.5–9) advertised in the Regulation of the Minister of Maritime Economy and Inland Navigation of July 12, 2019 (Journal of Laws 2019, item 1311). The reaction value strongly depends on granules stability during the leaching test, so the leaching of alkali ions could be a semi-permanent process (Su and Wong 2004).

The highest electrolytic conductivity was in the eluate from the 1⁰ leaching (9010 $\mu\text{S}/\text{cm}$), exceeding the save value (about 2500 $\mu\text{S}/\text{cm}$), what was established for plants (Ciesielczuk et al. 2018). The lowest one was noted for the eluate from the 2⁰ leaching (2950 $\mu\text{S}/\text{cm}$), slightly exceeding the limit value, while the eluate from the third leaching stage (1630 $\mu\text{S}/\text{cm}$) could be released to the environment without previous refinement. A worrying phenomenon is the strong salinity of the solution, particularly pronounced in the case of the 1⁰ leachate (Ciesielczuk et al. 2018).

When comparing concentrations of metals in the eluates (Table 1) with the limit values, presented in the aforementioned regulation, it can be stated that all the lixiviated elements are characterised with significantly lower values in comparison to the limited ones in the regulation. Three trace metals Cd 0.03 mg/dm^3 , Ni 0.04 mg/dm^3 i Pb 0.19 mg/dm^3) leached themselves in the same amount on every lixiviation stage, while the lixiviation of the others (Cr, Cu, Zn) was unequal (the biggest in the time 2⁰: Cr 0.043 mg/dm^3 , Cu 0.017 mg/dm^3 , Zn 0.025 mg/dm^3). There are no limit values for Li in the aforementioned Regulation of the Ministry of Environment of November 18, 2014. The lixiviation of Na and K was unequal,

Table 2. Loads of the determined indicators (mg/kg DM) in eluates from the brown coal ash

Tabela 2. Ładunki oznaczonych wskaźników (mg/kg s.m.) w eluatach z popiołu z węgla brunatnego

Indicator	q1	q2	q3	Q
	mg/kg DM			
Ni	0.40	0.33	0.24	0.97
Zn	0.10	0.20	0.018	0.318
Cd	0.30	0.25	0.18	0.73
Cu	1.250	0.139	0.084	1.473
Cr	0.41	0.35	0.18	0.94
Pb	1.90	1.60	1.14	4.64
Li	7.00	5.70	4.80	17.50
Na	738.0	588.0	487.2	1813.2
K	331.0	267.0	219.0	817.0

but the biggest in the 3⁰ of leaching, was 81.2 and 36.5 mg/dm³. All the concentrations are a result of non-biological leaching due to a strong alkali reaction and high EC parameter (Pathak et al. 2009). In the case of a strong alkali reaction, a lot of metals resources which are bound in relatively stable compounds will be not present in the leachate – hence there is no full environmental toxicity information (Zhao et al. 2018).

Concentrations of the studied elements serve as a calculation of the lixiviated loads from every single leaching stage (q_1, q_2, q_3) as well as their sum (Q) based of the formulas presented in the PN-EN 12457:2006 standard. For the reason, they were provided in mg/kg DM of very low numerical values, and not in g/kg DM as recommended in the PN.

Among trace elements, the biggest cumulative load is present in lead (4.64 mg/kg DM.), over three times smaller than (in comparison to Pb) copper (1.473 mg/kg DM), however the cumulative loads of the other trace elements do not exceed 1 mg/kg s.m (in the decreasing sequence: Ni – 0.97 mg/kg DM, Cr – 0.94 mg/kg DM, Cd – 0.73 mg/kg DM, Zn – 0.318 mg/kg DM) which confirms the previously obtained results due to leaching test of granules (Rosik-Dulewska et al. 2008). As far as macroelements are concerned, the biggest cumulative load is present in sodium (1813.2 mg/kg DM), and then (in the decreasing sequence) K (817.0 mg/kg DM), Li (17.5 mg/kg DM).

3. Qualitative content of trace elements in the brown coal ashes, conducted on the basis of sequential chemical extraction according to the BCR methodology

The total content of heavy metals in sewage sludge may be high, and exceed 400 mg/kg DM per element (Pöykiö et al. 2016), however the real mobile and semi-mobile contents are determined in accordance with the aforementioned methodology, ash samples were submitted to chemical extraction according to the BCR method (Table 3). In this way, in fraction I (metals attached with carbonates) Cr was most frequently indicated (2.61 mg/kg DM), next in the decreasing sequence: Cu (1.36 mg/kg DM), Ni (1.12 mg/kg DM), Zn (0.65 mg/kg DM), Cd and Pb (below the detection limit method). The high mobility of Ni was confirmed in the different types of research (ash from wood biomass) (Jukić et al. 2017).

In the fraction II (metals connected with the hydrated oxides of iron and manganate) Zn was most frequently indicated (24.03 mg/kg DM), then Cu in the decreasing sequence 17.79 mg/kg DM), Cr (7.84 mg/kg DM), Ni (7.06 mg/kg DM), Pb (2.89 mg/kg DM) as well as trace amounts of Cd – below the detection limit method. In these two first fractions Cd could be present in relatively high concentrations, what was observed in different investigations, which is the opposite to obtained results (Pöykiö et al. 2016).

In fraction III (metals attached with the organic matter and sulphides) Zn was marked most frequently (13.47 mg/kg DM), then Cu in the decreasing sequence (10.85 mg/kg DM), Ni (9.98 mg/kg DM), Cr (9.95 mg/kg DM), Pb (7.63 mg/kg DM). Others authors find copper as a dominant element in this fraction (Hei et al. 2016).

Table 3. The comparison of sequential chemical extraction BCR results and the sum of trace metals loads (Q) from the three-stage brown coal ash leaching test

Tabela 3. Porównanie wyników sekwencyjnej ekstrakcji chemicznej BCR i sumy ładunków (Q) metali śladowych z trójstopniowego testu wymywalności popiołów z węgla brunatnego

Sequential chemical extraction according to the BCR method						Leaching test
Metal	fraction I	fraction II	fraction III	fraction IV	Sum of loads fractions I–IV	Sum of eluted loads Q
	mg/kg DM	mg/kg DM	mg/kg DM	mg/kg DM	mg/kg DM	mg/kg DM
Cu	1.36	17.79	10.85	15.17	45.17	1.47
Zn	0.65	24.03	13.47	57.04	95.19	0.32
Cd	0	0	0	0	0	0.73
Ni	1.12	7.06	9.98	27.57	45.73	0.97
Pb	0	2.89	7.63	8.14	18.66	4.64
Cr	2.61	7.84	9.95	20.66	41.06	0.94

In fraction IV (metals connected with the mineral deposit) Zn (similarly to the previous fractions) was marked most frequently (57.07 mg/kg DM), next Ni in the decreasing sequence Ni (27.57 mg/kg DM), Cr (20.66 mg/kg DM), Cu (15.17 mg/kg DM), Pb (8.14 mg/kg DM).

Cd in all attachments was marked in trace amounts, which means – below the detection limit method.

To sum up the results of the sequential extraction according to BCR, it might be concluded that in fraction I (metals connected with carbonates) Cr is the the most dominant (2.61 mg/kg DM), while in the attachments marked as fraction II, III i IV – zinc, which was indicated in the biggest amounts in the attachments with silicates (57.04 mg/kg DM – fraction IV) and sequentially with hydrated iron and manganese oxides (24.03 mg/kg DM – fraction II), with organic matter (13.47 mg/kg DM – fraction III).

4. The comparison of results of an evaluation in respect of the influence of the brown coal fly ash on the natural environment, according to both of the applied chemical methods

The total content (as a sum of fractions I–IV loads – Table 3) was the highest for Zn (95.20 mg/kg DM), over twice lower (in proportion to Zn) for Ni (45.70 mg/kg DM), Cu (45.20 mg/kg DM), Cr (41.10 mg/kg DM), and much lower for Pb (18.70 mg/kg DM) and Cd (0 mg/kg DM) (Rosik-Dulewska et al. 2013; Pöykiö et al. 2016).

The total content (Table 3) of trace elements (as a sum of the fractions I–IV loads) received as a result of the chemical extraction sequential analysis (with the use of chemical compounds solutions of differentiated lixiviation power) were definitely higher in comparison to the sum of lixivated/received loads as a result of the conducted leaching test.

5. The percentage participation of metals in fractions, according to the sequential chemical extraction BCR in brown coal ash

When analyzing the percentage participation of metals marked according to the BCR methodology (Table 4), in the attachments as fractions I–IV:

- ◆ With carbonates (fraction I) the highest percentage accrues to Cr (6.36%), a lot lower for Cu (3.01%), Ni (2.45%), Zn (0.68%), and the lowest for Cd and Pb (0% each)
- ◆ With hydrated iron and manganese oxides (fraction II) the highest percentage accrues for Cu (39.38%), lower for Zn (25.24%), Cr (19.09%), Pb (15.49%), Ni (15.44%), and the lowest for Cd (0%). The heavy metal content in high mobile fraction I is low and the semi mobile fraction II is moderate, which is optimal from the plant uptake point of view (Rosik-Dulewska et al. 2013).
- ◆ With organic matter as well as with sulphides (fraction III) the highest percentage accrues for Pb (40.89), lower for Cr (24.23%), Cu (24.02%), Ni (21.82%), Zn (14.15%), and the lowest for Cd (0%).

Table 4. The percentage participation of trace elements in fractions I–IV of the sequential chemical extraction BCR in the brown coal ash

Tabela 4. Procentowy udział pierwiastków śladowych we frakcjach I–IV sekwencyjnej ekstrakcji chemicznej BCR w popiołach z węgla brunatnego

Sequential chemical extraction according to the BCR method						
Metal	fraction I	fraction II	fraction III	fraction IV	sum I–III	sum II–III
	%	%	%	%	%	%
Cu	3.01	39.38	24.02	33.58	66.42	63.40
Zn	0.68	25.24	14.15	59.92	40.08	39.39
Cd	0	0	0	0	0	0
Ni	2.45	15.44	21.82	60.29	39.71	37.26
Pb	0	15.49	40.89	43.62	56.38	56.38
Cr	6.36	19.09	24.23	50.32	49.68	43.32

- ◆ With the mineral deposit (fraction IV) the highest percentage accrues for Ni (60.29%), lower for Zn (59.92%), Cr (50.32%), Pb (43.62%), Cu (33.58%), and the lowest for Cd (0%). Results of fraction IV was partly confirmed in research with hard coal ash – Cr and Pb was mostly determined as no-mobile ions (Krgović et al. 2014).

To sum up the percentage of metals in the attachments marked as fractions I–IV it can be concluded that (fraction I) Cr was attached with carbonates in the largest amounts (6.36%), with hydrated iron and manganese oxides (fraction II) Cu (39.38%), with organic matter and sulphides (fraction III) Pb (40.89%), and with the mineral deposit (fraction IV) Ni (60.29%) and Zn (59.92%).

As it results from the metals' percentage in the attachments marked as fractions I–III (available also for ecosystem, although in a differentiated level), copper was mainly attached with hydrated iron and manganese oxides (fraction II – 39.38%) and in a slightly smaller amount with mineral deposit (fraction IV – 33.58%), however zinc, nickel, lead and chrome with mineral deposit (fraction IV), and cadmium in all fractions was marked below the detection limit method (0%).

Conclusions

While comparing the results of the research on the brown coal ashes received from a leaching test as well as from the sequential chemical extraction (according to the BCR methodology), as far as the influence on the environment is concerned it can be stated that:

1. Concentrations of the trace elements analyzed in the other three leaching stages are significantly lower than the ones described in the aforementioned regulation, thus in this scope they do not constitute any danger neither for water nor for the soil environments.
2. The sequential analysis of chemical extraction carried out according to the BCR method allows for the evaluation of the right influence of ashes/wastes on the environment indicates are the following facts:
 - ◆ the sum of loads (mg/kg DM) of the indicated trace elements in the eluates from the leaching tests is often lower than the amount of the lixiviated one only in the fraction described as the most available for the environment,
 - ◆ metals connected in the attachments as fraction II or III in the described/determined in the soil environment conditions can also be released, apart from that they constitute a total from 37.2% Ni to 63.4% Cu of the complete sum of loads from fractions I–IV,
 - ◆ Zn, Ni, Pb and Cr are mainly bound in the combinations unavailable for the environment (fraction IV), moreover they constitute from 43.62% (Pb) to 60.29% (Ni) of the sum of loads from fractions I–IV.
3. The research carried out proves the fact that the leaching tests required in the regulation used for wastes before being applied to the environment, point only at those contents which we achieve after the first stage of the sequential chemical extraction, that is – metals bound interchangeably that do not indicate full danger.

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**COMPARATIVE ANALYSIS OF THE EVALUATION OF THE INFLUENCE OF WASTE
ON THE ENVIRONMENT DEPENDING ON THE APPLIED RESEARCH METHOD
(ON THE EXAMPLE OF BROWN COAL ASH)**

Keywords

leaching test, lignite ashes, heavy metals, sequential chemical extraction, BCR

Abstract

The problem of the migration of metal ions in the environment remains a current problem in light of the quality of obtained crops. The necessity of more and more frequent use of alternative sources of biogens in the form of waste substances, poses a threat of loading significant amounts of metals into the soil – including heavy metals harmful to human health and life.

The article discusses a significant problem, namely the comparison of the results of the environmental impact of waste, obtained on the basis of legally authorized leaching tests (three-stage leaching test according to PN-EN 12457:2006), with results obtained from sequential chemical extraction (performed in 4-step chemical extraction developed and recommended in European Union countries by Communities Bureau of References – BCR).

The study covered an investigation of industry fly ash from the combustion of lignite, in which Cu, Zn, Cd, Ni, Pb, Cr, Na, K, Li concentrations and loads were calculated. A mobility of analyzed elements was established on this basis. From heavy metals, the highest values in fraction I were noted for nickel and copper and zinc as well as nickel were noted for fraction IV. Peaking values of electrolytic conductivity in eluates was created by high concentrations of macroelements (Na and K). These tests confirm that the leaching tests used for their application in the natural environment indicate such concentrations at the highest levels that can be obtained at the first or second stage of sequential chemical extraction, and thus their proper full environmental impact is not known.

**ANALIZA PORÓWNAWCZA OCENY WPLYWU ODPADÓW NA ŚRODOWISKO
W ZALEŻNOŚCI OD ZASTOSOWANEJ METODY BADAWCZEJ
(NA PRZYKŁADZIE POPIOŁU WĘGLA BRUNATNEGO)**

Słowa kluczowe

testy wymywalności, popioły lotne, metale ciężkie, ekstrakcja sekwencyjna,
węgiel brunatny, BCR

Streszczenie

Problematyka obiegu jonów metali w środowisku pozostaje aktualnym problemem w świetle jakości uzyskiwanych plodów rolnych. Konieczność coraz częstszego wykorzystywania alternatywnych źródeł biogenów w postaci substancji odpadowych stwarza zagrożenie wnoszenia do gleb znacznych ilości metali – w tym szkodliwych dla zdrowia i życia człowieka – metali ciężkich.

W artykule poruszono istotny problem, jakim jest porównanie wyników oceny oddziaływania odpadów na środowisko uzyskanych w oparciu o wykonanie prawnie usankcjonowanych testów wymywalności (trzystopniowy test wymywalności wg PN-EN 12457:2006), z wynikami uzyskanymi z badań sekwencyjnej ekstrakcji chemicznej (w pracy wykonano 4-stopniową ekstrakcję chemiczną opracowaną i zalecaną w krajach Unii Europejskiej przez Communities Bureau of References – BCR).

Badaniom poddano popiół lotny ze spalania węgla brunatnego w przemyśle energetycznym, w którym oznaczono stężenia Cu, Zn, Cd, Ni, Pb, Cr, Na, K, Li. Na tej podstawie określono mobilność analizowanych pierwiastków. Najwyższe stężenia we frakcji I zanotowano dla chromu i miedzi, zaś w pozostałości (frakcja IV) dla cynku i niklu. Wysokie wartości przewodności elektrolitycznej eluatów były wynikiem znacznych zawartości makropierwiastków (Na i K). Badania te potwierdzają, że testy wymywalności stosowane na potrzeby ich aplikacji w środowisku przyrodniczym wskazują co najwyżej takie stężenia, jakie uzyskujemy na pierwszym ewentualnie drugim stopniu sekwencyjnej ekstrakcji chemicznej. Co za tym idzie, nie poznajemy ich właściwego pełnego oddziaływania na środowisko.