Mineralogical, Chemical, and Leaching Characteristics of Coal Combustion Bottom Ash from a Power Plant Located in Northern Poland

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Abstract

The present research is focused on chemical and mineralogical characterization of bottom ashes produced during coal combustion in a power plant operating in northern Poland. On the basis of these results we estimate a potential environmental hazard and try to find a possible application for studied materials. Bulk chemical composition of all studied bottom ash samples is homogenous and SiO_2 and Al_2O_3 are the major components of samples and together with Fe_2O_3 represent more than 70 wt. %. All ashes were thus classified as type F ashes. CaO and SO_3 concentrations are relatively low and reach up to 3.1 and 0.32 wt. %, respectively. The total concentrations of trace elements in the studied bottom ash samples are generally lower than those reported for the coal from different countries. The highest concentration of trace elements was noted for Co and Pb (up to 84 and 76 mg·kg⁻¹, respectively), and the lowest for Hg and Se (up to 0.2 and 2 mg·kg⁻¹). Studied samples of bottom ash are mostly composed of mullite and quartz with some minor amounts of hematite and traces of calcite. Two types of leaching experiments (using distilled water and 0.05 mol/L of EDTA solution) show that the mobility of select inorganic pollutants (Co, Cu, As, Ni, Zn, and Pb) is relatively low and together with the results of total element concentration in bottom ash indicate that the potential risk associated with the release of trace elements from studied wastes is negligible. Therefore, studied wastes could be successfully used as a secondary raw material.

Keywords: combustion residues, EDTA extraction, environmental impact, metal(loid) mobility

Introduction

Combustion of coal leads to the formation of large amounts of wastes (CCRs – coal combustion residues), of which the most important are: fly ashes, bottom ashes, boiler slags, and products resulting from dry or wet flue gas desulphurization. In 2009 the European Coal Combustion Products Association (ECOBA) estimated that total annual production of CCRs in the European Union was close to 100 million tons. Average utilization rate of CCRs in 2009

was at the level of around 50%, but due to the fact that these wastes are often successfully used as secondary raw materials this rate will probably increase in the forthcoming years.

Energy production in Poland is based mainly on coal burning, which causes formation and disposal of large amounts of combustion residues (Table 1). Nowadays, the majority of wastes generated as a result of coal burning is reused (especially fly ash; Table 1). However, hundreds of millions of tons of wastes associated with coal combustion that could be used as raw materials are still present in landfills (Table 1). It is therefore important to study these

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Table 1. Coal production in 2000, 2005, and 2011 and the generation and disposal of wastes associated with coal combustion (data from Statistical Yearbook of the Republic of Poland 2012).

Coal production [mln t]			
Type of coal/year	2000	2005	2011
Hard coal	103	97.9	76.5
Lignite	59.5	61.6	62.8
Wastes associated with coal combustion			
Type of waste	Waste generated in 2011 [mln t]	Waste landfilled and temporarily stored in 2011 [% of waste generated]	Total amount of waste landfilled by the end of 2011 [mln t]
Dust-slag compounds from wet treatment of furnace waste	10.4	87	258
Coal fly ash	4.5	0.4	19
Bottom and furnace ash, boiler slag	2.6	4	19.2

wastes, both in terms of their use as well as potential impact on the environment.

CCRs may constitute a marketable raw material and can be used as construction materials, as cement and concrete additives [1-5], in the production of synthetic zeolites [6, 7], and in agriculture [8, 9]. However, due to the presence of some inorganic components (e.g., trace elements) similar as in post flotation wastes [10, 11], these wastes also can be a source of serious pollution [12]. Therefore, the environmental impact of these materials should be investigated in detail.

Numerous studies deal with the mobility of trace metals and metalloids from coal combustion fly ash [13-16], smelter fly ash, and slag [17, 18]. Most of the studies focusing on fly ash from coal combustion indicate that these wastes are rather environmentally safe and may be used, for example, in agriculture, civil engineering, and in extraction of valuable materials [13]. However, fly ash generated during coal burning may be up to several times more radioactive than feed coals [19]. Fly ash produced by the smelting industry are known to be environmentally hazardous due to the presence of relatively high concentrations of trace elements that can be easily mobilized, especially in acidic soils [20]. Nevertheless, studies focusing on the characterization and potential environmental impact of bottom ash and slag generated during coal combustion are relatively rare [12, 21]. These materials constitute a minority of waste mass generated by heat and power plants and concentrations, and the mobility of potential contaminants (e.g., trace metals and metalloids) are generally lower than in fly ash [21].

Distribution of potentially hazardous trace elements among different types of coal combustion waste is variable and depends on the characteristics of coal, solid speciation of a given element in coal, combustion conditions, and volatility of elements [22]. Highly volatile elements (e.g., Hg) are rather connected with flue gases and/or fly ash than with bottom ash and/or boiler slag [21], thus the latter appear to be less hazardous for the environment. Any use of combustion residues in any industry should therefore be

preceded by a detailed study of these wastes in order to evaluate the potential environmental risk.

Nowadays, the intention of the whole industry should be to reuse as much waste as possible. Therefore, in this study we analyze chemical and phase composition of bottom ash samples generated during coal combustion in the Dolna Odra power plant and disposed of in a landfill from 1990 to 2008. The main objective of this paper is to evaluate the potential environmental risk related with the release of trace elements from these wastes. For this purpose we use two single extraction methods and try to indicate whether studied bottom ash could be a marketable secondary raw material or constitute a potential source of pollution for the environment.

Materials and Methods

Site Description and Sampling

As a result of electricity production the Dolna Odra power plant generates annually about 500-600,000 tons of wastes such as fly ash, bottom ash, and slag. Fly ash from electrofilters (about 250-280,000 tons per year) is pneumatically transferred to the distribution stations. Subsequently these materials are used in the construction industry as an additive to concrete as well as for reclamation and grading of the land. Other wastes (bottom ash and slag) are transported through a hydraulic method to a landfill where they are stored. The area of ash disposal is generally flat and height differences in various parts of the site do not exceed 0.3 m. The landfill is located on Holocene peats (with a high degree of humification) having a maximum thickness of 3 m underlined by fluvioglacial sands and gravels.

Samples of bottom ash selected for this study resulted from pulverized coal combustion and the maximum combustion temperature reached up to 1,600ºC. Studied bottom ash comes from a wet disposal where it was deposited in the period from 1990 to 2008. The sampling site is located in section 4bb in the northwestern part of the ash disposal

(Fig. 1). During fieldwork a 2-meter deep prospecting shaft was excavated and five representative samples taken at various depths along the vertical profile: 0.4 m – sample SzB1, 0.7 m – sample SzBA, 1 m – sample SzB2, 1.7 m – SzB3, and 1.9 m – SzB4.

Representative splits of bottom ash samples were prepared for chemical and mineralogical analyses as well as for single chemical extractions.

Analytical Methods

Bulk chemical composition of bottom ash was determined on pulverized samples by melting the sample with $LiBO_2\text{-}Li_2B_4O_7$, followed by dissolution of the residue in nitric acid and analyses by ICP-AES for major elements and ICP-MS for trace elements (ACME Analytical Laboratory, Vancouver, Canada). Total sulfur and carbon contents in bottom ash were determined by the LECO combustion analysis. Loss on ignition (LOI) was analyzed by sintering of the sample at 1,000ºC.

Mineral compositions of studied samples was identified using the X-ray powder-diffraction (XRD) with CoKα radiation. Diffraction patterns for all samples were recorded from 4º to 90º 2θ, at a rate of 1.2º 2 θ min^{-1} with a Siemens D5005 diffractometer housed at the Institute of Geological Sciences, University of Wrocław. Polished thin sections of studied samples were observed using a polarizing microscope and a scanning electron microscope (SEM) coupled with energy dispersive x-ray spectrometry (EDS; Vega LSU Tescan) at the Wrocław University of Technology.

Two selective single extraction procedures were used in this study. For each extraction a separate aliquot of the same sample was used. Both procedures were intended to extract the most mobile fractions of metals present in studied bottom ash. Extractions were performed on pulverized and homogenized samples of bottom ash at room temperature (21ºC±2ºC) in pre-cleaned polypropylene bottles.

Experiments were conducted in triplicate and procedural blanks were prepared for each leaching solution.

First extraction was performed using distilled water as a leaching solution and an easily mobilizable fraction was targeted. Extractions was conducted at a liquid/solid ratio of 10 (20 g of sample in 200 mL of distilled water). The solution was continuously agitated for 2 h on a table shaker. Afterward the suspensions were centrifuged for 10 min (1,500 min^{-1}) and the leachates were analyzed.

The second extraction was done using EDTA as a leaching solution according to a procedure described by Quevauviller [23]. The targeted fraction was a slowly mobilizable fraction representing metals that may be potentially transferred from soil to plants (bioavailable fraction). Extractions was conducted at a liquid/solid ratio of 10 (5 g of sample in 50 mL of 0.05 mol/L EDTA solution). The solution was continuously agitated for 1h on a table shaker. Afterward the suspensions were centrifuged for 10 min (1,500 min^{-1}) and the leachates were analyzed.

Metal concentrations in leachates from the extraction experiments were analyzed by flame atomic absorption spectrometry (FAAS) and/or graphite furnace atomic absorption spectrometry (GF-AAS) using a GBC Avanta instrument (Hydrochemical Laboratory of the Institute of Geography, University of Wrocław).

Results and Discussion

Chemical and Mineralogical Properties of Ash

Bulk chemical composition of all studied bottom ash samples is homogenous (Table 2). SiO_2 and Al_2O_3 are the major components of samples and together with Fe_2O_3 represent more than 70 wt. %, therefore all ash was classified as type F. CaO and SO_3 concentrations are relatively low and reach up to 3.1 and 0.32 wt. %, respectively (Table 2).
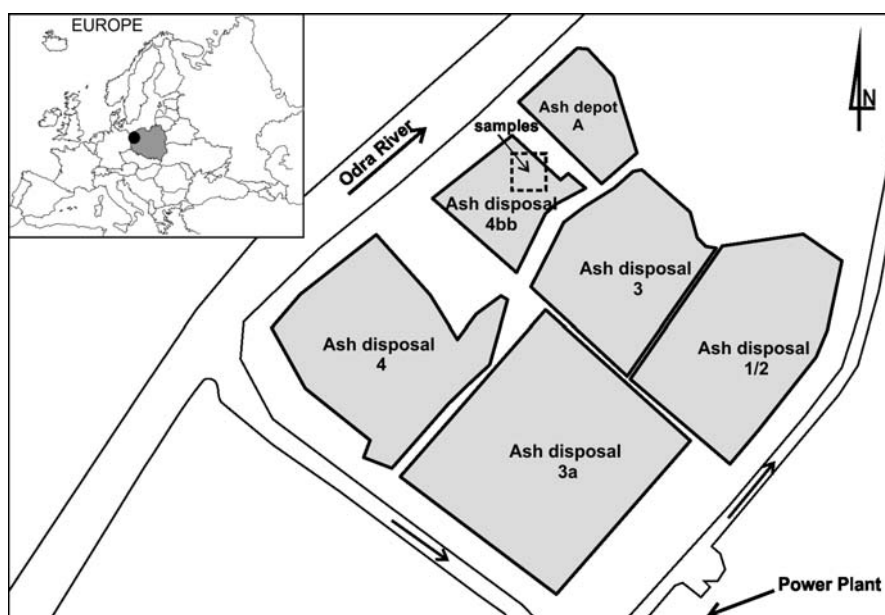

Fig. 1. Schematic picture showing location of power plant, position of ash disposals, and sampling area.

Table 2. Chemical composition of bottom ash samples.

Element/ Sample ID	SZA	SZB1	SZB2	SZB3	SZB4
Major elements [wt. %]					
SiO_2	50.16	50.05	53.08	52.41	52.77
Al_2O_3	24.02	26.90	26.20	25.62	26.78
Fe_2O_3	6.08	5.43	5.61	5.02	5.03
MgO	2.60	2.50	2.24	1.84	2.08
CaO	3.06	3.00	2.60	1.93	2.32
Na_2O	0.80	1.18	0.72	0.61	0.81
K_2O	3.01	3.30	3.21	3.17	3.28
TiO_2	0.97	1.08	1.06	0.99	1.10
P_2O_5	0.41	0.63	0.39	0.28	0.48
SO_3	0.17	0.32	0.15	0.10	0.20
LOI	8.7	5.4	4.4	7.8	4.9
Total	99.93	99.60	99.55	99.74	99.61
Trace elements [mg·kg⁻¹]					
As	12.6	40.6	18.8	5.5	26.8
Cd	0.2	0.4	0.3	0.1	0.4
Co	66.9	62.8	52.1	84.4	52.5
Cu	33.0	43.2	24.2	14.9	33.1
Hg	0.24	0.20	0.05	<0.01	0.18
Ni	29.7	42.6	26.1	17.6	30.2
Pb	22.4	43.0	22.5	9.6	34.7
Sb	2.4	5.3	3.1	1.0	4.1
Se	1.8	1.5	<0.5	<0.5	0.9
Zn	44	76	48	21	72

Compared to other bottom ash produced during pulverized coal combustion [13], the studied ash have higher LOI (loss on ignition) content (Table 2), which makes these wastes not suitable for cement and concrete production. The highest concentration of trace elements was noted for Co and Pb (up to 84 and 76 mg·kg⁻¹, respectively), and the lowest for Hg and Se (up to 0.2 and 2 mg·kg⁻¹, respectively; Table 2). The total concentrations of trace elements in the studied bottom ash samples are generally lower than those reported for coal from different countries [24], except for Cu, Ni, Pb, and Zn. As, Hg, Sb, and Se are known to be highly volatile trace elements that have the affinity to condense rather on the surface of fly ash particles than in the bottom ash [21]. The major environmental problem related to studied bottom ash should involve the mobility of other so-called heavy metals such as: Co, Ni, Cu, Zn, and Pb.

Combustion in the power plant furnace leads to transformation of coal minerals, represented mainly by quartz, phyllosilicates (including kaolinite, illite etc), sulfides (e.g., pyrite), and carbonates (e.g., calcite) to newly formed phases that made up the coal combustion residues (bottom and fly ash, boiler slag). This conversion process is complex because of numerous chemical interactions taking place between solids, liquids, and vapors at high temperatures in a very short time period [13]. Studied samples of bottom ash are mostly composed of mullite and quartz with some minor amounts of hematite and traces of calcite (Figs. 2, 3A). Elevated background of collected X-ray powder diffraction patterns of all samples a presence of an aluminosilicate glass is another major component of bottom ash (Fig. 2). These findings have been confirmed by SEM-EDS observations of studied samples, which revealed the presence of numerous spherical glassy particles composed mostly of silica and alumina (Figs. 3A, C). The formation of aluminosilicate glass and mullite takes place around 1,000-1,100ºC and major substrates of this reaction are phyllosilicates [13]. Mullite is stable between 1,100ºC and
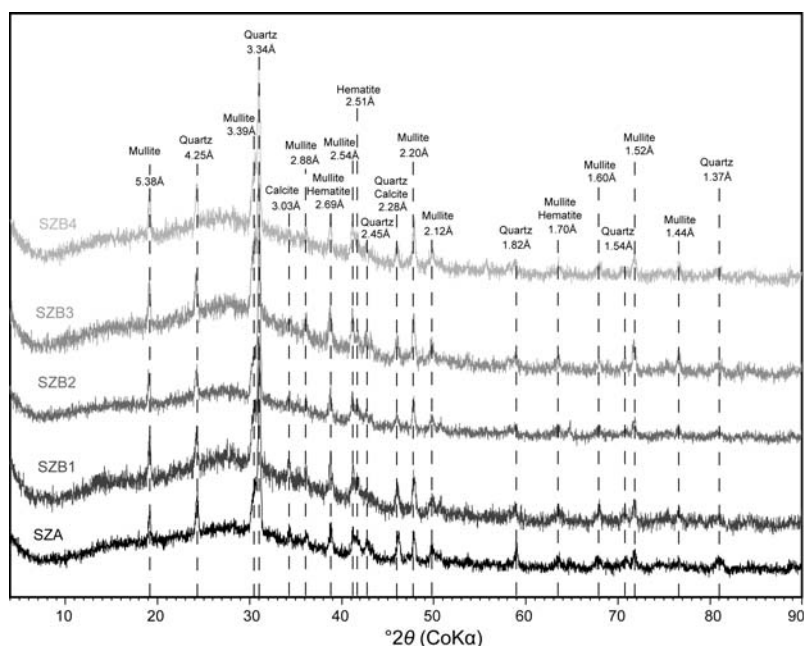

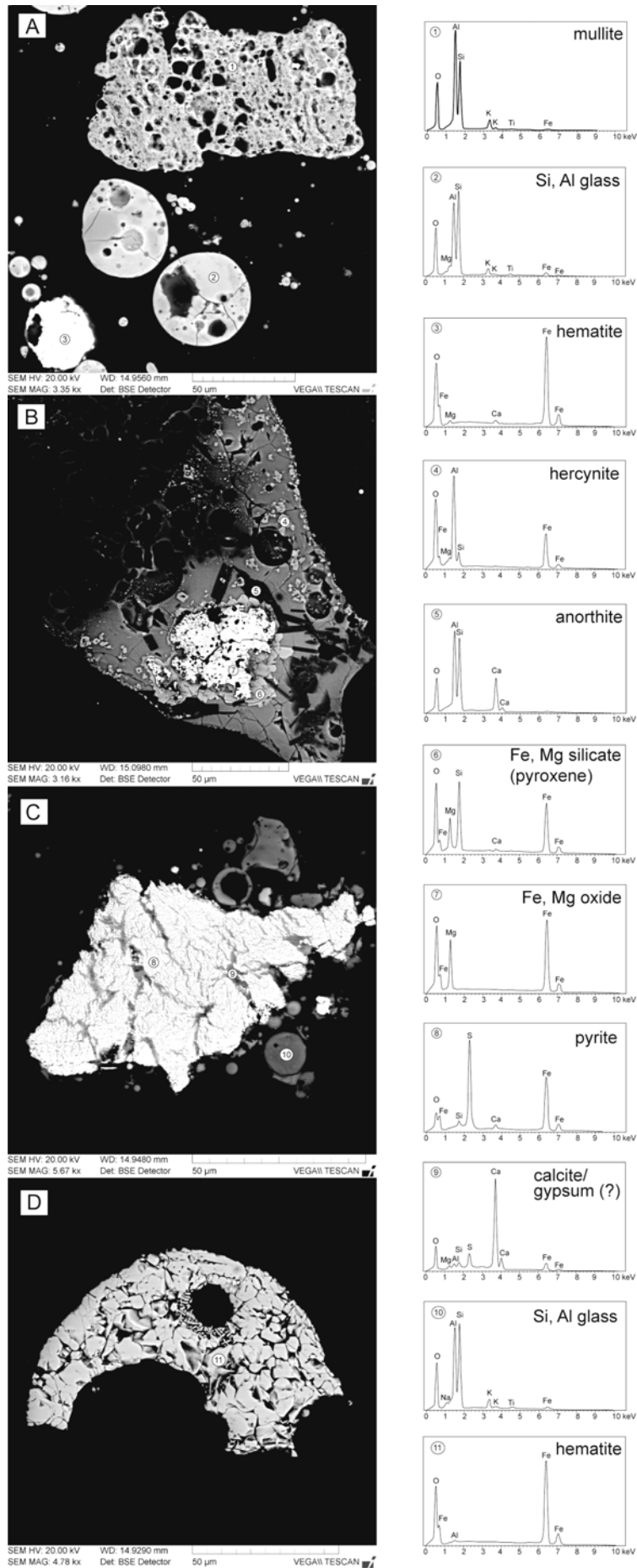Fig. 2. X-ray powder diffraction patterns presenting mineral composition of studied bottom ash samples.

Fig. 3. SEM-BSE images of the studied ash samples with corresponding EDS spectra and interpretation of the analyzed phases.

Table 3. Metal(loid) concentrations in leachates obtained in two mobility experiments on ash samples.

Sample	Initial metal(loid) concentration in ash sample [mg·kg⁻¹]	Metal(loid) concentration extracted using distilled water [µg·kg⁻¹]	Metal(loid) concentration extracted using EDTA solution [mg·kg⁻¹]	Proportions of metal(loid)s extracted by EDTA solution [%]
Cobalt				
SZA	66.9	< d.l.	6.36	9.51
SZB1	62.8	< d.l.	2.53	4.02
SZB2	52.1	< d.l.	2.77	5.32
SZB3	84.4	< d.l.	15.99	18.94
SZB4	52.5	< d.l.	1.80	3.43
Nickel				
SZA	29.7	13.68	3.90	13.13
SZB1	42.6	34.58	5.39	12.66
SZB2	26.1	10.92	4.22	16.18
SZB3	17.6	9.0	2.57	14.62
SZB4	30.2	7.75	4.72	15.63
Copper				
SZA	33.0	0.02	8.73	26.45
SZB1	43.2	0.28	11.79	27.30
SZB2	24.2	0.10	6.86	28.35
SZB3	14.9	0.24	4.11	27.53
SZB4	33.1	0.16	9.13	27.59
Zinc				
SZA	44	1.90	6.26	14.23
SZB1	76	15.06	9.43	12.41
SZB2	48	2.85	9.60	19.99
SZB3	21	2.37	3.90	18.57
SZB4	72	9.15	10.46	14.53
Arsenic				
SZA	12.6	97.41	0.84	6.69
SZB1	40.6	190.77	0.60	1.47
SZB2	1.8	156.37	0.97	5.14
SZB3	5.5	147.17	0.79	14.42
SZB4	26.8	214.09	1.30	4.86
Lead				
SZA	22.4	< d.l.	1.71	7.62
SZB1	43.0	< d.l.	5.47	12.71
SZB2	22.5	< d.l.	5.82	25.85
SZB3	9.6	< d.l.	0.71	7.40
SZB4	34.7	< d.l.	5.0	14.42

< d.l. – below detection limit

1,500ºC and it may coexists with its molten phase and recrystallizes during cooling [25]. Quartz is still present in the studied bottom ash samples as a major phase, although it was noted that it transforms to glass at 1,300ºC and under oxidizing conditions [26]. This may be explained by:

(i) Only partial melting of quartz because of the short residence time of its particles in a furnace
(ii) A temperature below 1,300ºC in a furnace.

Hematite present in studied bottom ash samples was formed through decomposition of sulfides presumably under oxidizing conditions [27]. Although this phase is stable under 1,400ºC, but it may start to convert partially to a glassy phase at around 1,000º [13]. Except for major (e.g., mullite, hematite) phases identified by XRD, some other high-temperature phases were also observed within studied samples. These phases are represented by silicates having chemical composition close to anorthite, pyroxene, and oxides (e.g., hercynite; Fig. 3B). Traces of calcite were identified in almost all studied samples of bottom ash (Fig. 2). Decomposition of carbonates takes place at relatively low temperatures (below 850ºC), thus it is unlikely that this phase could not be heated enough to decompose. Calcite forms rather as a result of partial carbonatization of CaO from ash with moisture and atmospheric CO_2. Furthermore, SEM-EDS observations allowed us to identify several grains of pyrite within studied samples (Fig 3B). This suggests that part of this coal mineral was only partially transformed during combustion. Pyrite crystals occurring in studied samples are highly fractured and altered as a result of (1) combustion and (2) weathering of ash at the disposal site. The latter is manifested by the presence of secondary minerals (presumably gypsum or/and calcite; Fig. 3B). Sulfides are very important from an environmental point of view because their dissolution causes acid mine drainage. However, in studied samples the amount of sulfides is low, thus the negative environmental effects related to sulfide dissolution are negligible.

Leaching of Trace Elements

The leaching experiment using distilled water solution aims to show an easily mobilizable fraction of trace elements. The results of this extraction indicate that mobilization of trace elements from ash was minimal using distilled water as a leaching solution (Fig. 3, Table 3). The concentrations of all measured trace elements are of several orders of magnitude lower in distilled water leachates than those observed in the bulk ash samples (Fig. 3, Table 3). Among all analyzed trace elements, As is the most abundant and its concentrations exceed 200 µg·L⁻¹ in the distilled water leachates. Such behavior of this element could be explained by high affinity of As to hydrous iron oxides [28], which may form in studied samples of bottom ash as a result of hematite transformations. Ni and Zn concentrations in water leachates reach up to 35 and 15 µg·L⁻¹, respectively. These elements may also be removed from hydrous iron oxides by distilled water solution [29]. Concentrations of other measured elements are very low and do not exceed 0.3 µg·L⁻¹ in the case of Cu or 0.1 µg·L⁻¹ in the case of Co and Pb.

Chemical extraction using 0.05 mol/L EDTA solution at pH 7 determines a slowly mobilizable fraction of trace elements that may be captured by plants [23]. The results of the EDTA extraction for the studied bottom ash samples show ranges of element mobility and some differences between individual samples (Fig. 3, Table 3). Cu has the highest EDTA extractability from 26.5 to 28.5% of total concentration and As the lowest from 2 to 14% of total concentration (Fig. 3, Table 3). Cu is known to form specific complexes with soil organic matters [30], which may explain higher EDTA extractability of this element. Pb has the highest proportions of EDTA-extractable fraction reaching 26% of total concentration in one sample. In other samples these proportions range from 8 to 15%. Proportions of EDTA extractable fractions of Zn and Ni are similar and range from 12 up to 20% of total concentration. Co has generally low proportions of EDTA-extractable fraction (below 10%), but in one sample it reaches up to 19% of total concentration.

Based on results of the mobility experiment using EDTA extraction, analyzed trace elements can be set as follows from the most to least mobile: Cu > Zn ≥ Ni > Pb > Co > As.

Both leaching experiments together with the results of total element concentrations in bottom ash indicate that the potential risk associated with the release of trace elements from studied wastes is negligible.

Conclusions

Coal combustion for the purposes of power and heat production involves the generation of large quantities of wastes such as: fly ash, bottom ash, and slag. They are very often economically used and consist of valuable raw materials for many applications such as cement and concrete production, soil and waste treatment, extraction of precious metals, etc. However, these wastes may also contain con-
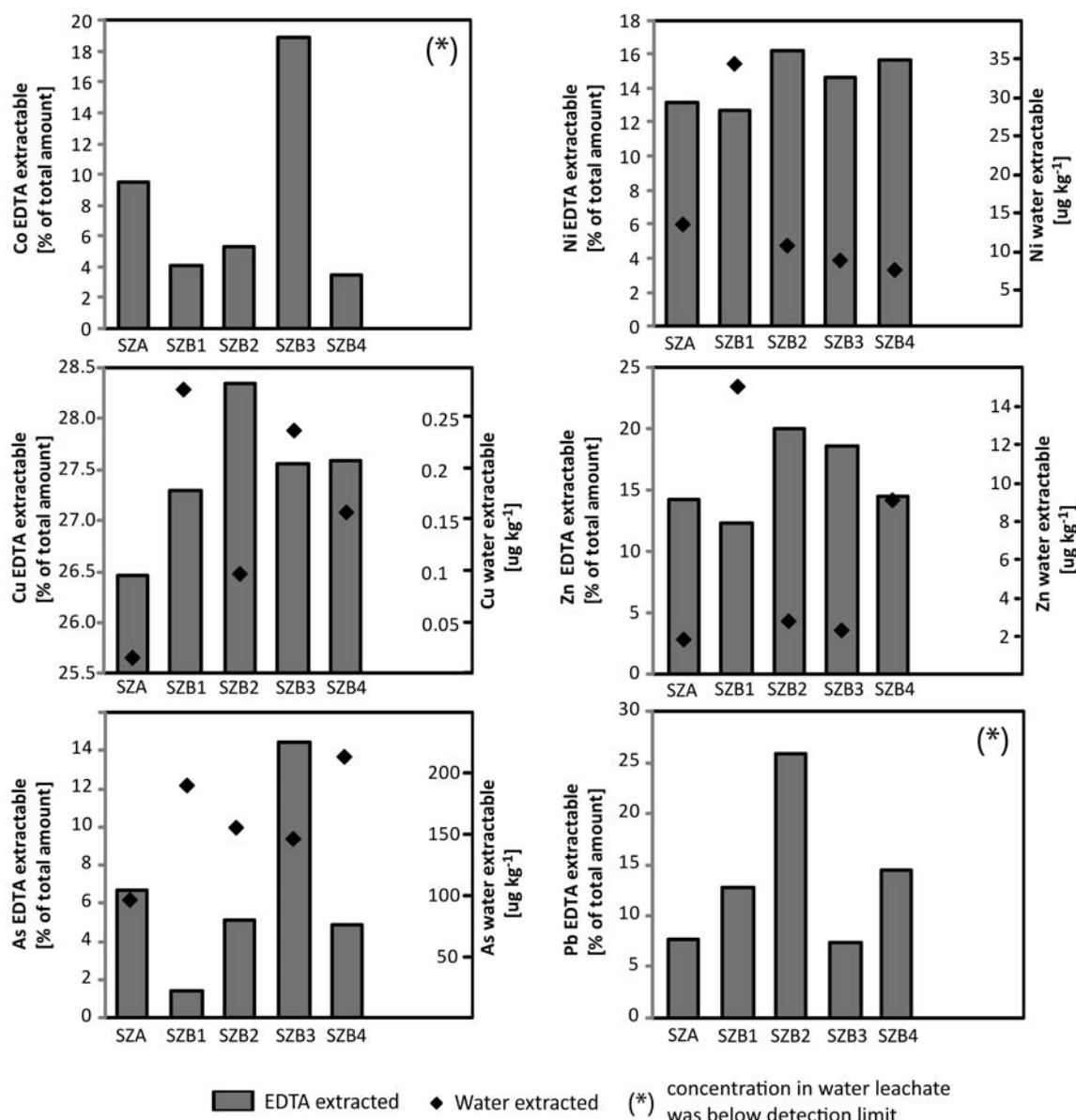

Fig. 4. Results of two single extraction experiments conducted for studied bottom ash samples.

siderable concentrations of toxic pollutants that can be leached out and contaminate surrounding soils and waters. For this reason, before use of coal combustion wastes an environmental study should be performed in order to determine the chemical characteristics and potential leachability of pollutants from these materials.

In the present study mineralogical and chemical analyses of bottom ash samples are coupled with leaching tests to indicate potential environmental risks related to studied wastes. The results show that studied materials do not contain important concentrations of inorganic pollutants, and also the potential mobility of select trace elements is relatively low. This indicates that bottom ash from the Dolna Odra power plant is environmentally inert and may constitute a valuable raw material. On the basis of our investigation we conclude that studied material is rather not suitable for concrete or ceramic production due to the relatively high LOI content. However, because of relatively low concentrations and mobility of inorganic pollutants it might be successfully used for the purposes of geoengineering as a secondary raw material. Parallel to our research we conducted another study aimed at the characterization of technical properties of bottom ash in order to find the best application for the studied wastes.

Acknowledgements

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