

Assessment of heavy metals leaching from fly ashes as an indicator of their agricultural use

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ABSTRACT

This paper attempts to assess the suitability of fly ashes from the combustion of solid fuels for agricultural development. The analyzed area of ash collection for research was the commune of Choroszcz in north-eastern Poland. The purpose of the study was to assess the pH and electrolytic conductivity of fly ashes from the combustion of solid fuels and to determine the amount of heavy metals leaching from water extracts of the ashes tested. Based on the results obtained, it was found that the content of heavy metals in aqueous fly ash extracts was affected by the combustion method and the type of fuel used. Distribution of heavy metals in the tested samples varied; the highest content was found in water extracts from ashes derived from combustible material, which is coal. It was found that fly ash has the highest leaching ability in the case of heavy metal – zinc. In addition, their alkaline nature has a significant impact on the possibility of agricultural use of fly ash.

Keywords: Fly ash; Heavy metals; Agricultural development

1. Introduction

Ashes as by-products of combustion are very widely used in various fields of the economy. In many countries, the possibility of mass consumption of fly ash is increasingly being sought. Their amount increases every year, therefore there is a need to find the appropriate way of their use. In recent years in Poland, their economic use is estimated at around 60% [1,2]. Due to the physical, chemical, and mineralogical composition of ash, the direction of its utilization can be different [3]. Extensive use of fly ash is possible due to their current status as a non-hazardous product or waste. Extensive research involving ashes gives the possibility of increasingly widespread and constantly expanding their use in many industries.

Fly ash is currently an indispensable component in numerous technological solutions [4,5]. High fineness, chemical, and phase composition (similar to mineral clay raw materials) and reactivity, especially pozzolanic activity, are the features that determine their wide use in construction [2,6,7]. Fly ash management is also carried out as the production of the filter and fireproof materials. The resulting energy wastes are increasingly used in environmental engineering as adsorbents for waste gas purification, among others: CO_{γ} , NO_{γ} [8]. Fly ash, being a source of silicon, aluminum, iron, nickel, gallium, germanium, and vanadium, is used for the recovery of valuable metals, but also for the synthesis of mesoporous aluminosilicates, that is, synthetic zeolites. In addition, fly ash is used for water and wastewater treatment [9]. One of the ways of managing the fly ash in this field is their transformation into sorbents which are zeolites [9]. They are used to remove heavy metals (mercury, lead, cadmium, nickel, copper, zinc, chromium), semi-metals (arsenic, boron), ammonium ions, phosphates, pigments and other organic compounds from solutions. It is worth mentioning that zeolites are also widely used in

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other fields, that is, chemical industry, medicine, environmental protection, microelectronics, optics, agriculture, and construction [10–13]. Fly ashes have good adsorption properties. They adsorb well soluble heavy metals such as zinc, lead, cadmium, and chromium [14]. In the results of research conducted by [14] on samples of brown coal and hard coal ashes, it was shown that increasing the pH increases the efficiency of heavy metal adsorption, that is, Zn, Pb, Cr, and Cd. When reaching a pH of 8, an efficiency of over 95% was obtained for each of the heavy metals tested, regardless of the concentration of the solution.

Waste from combustion, due to the presence of microand macroelements, is also used in agriculture, for example, for land reclamation, deacidification, composting, and fertilization as well as soil stabilization [13]. Ashes added to the soil improve its physical properties, increasing the sorption complex, water absorption, and reducing its volumetric weight. They also have a positive effect on soil microbiological processes. Ashes are not only a source of calcium and magnesium but also provide plants with trace elements that are easily absorbed. Agricultural ash management is possible due to the production of composts, in which they are the main component. Ash has been used for many years for fertilizing purposes, and primarily as calciummagnesium fertilizer [15]. In addition, brown coal ashes were used as calcium fertilizer for the remediation of soils containing large amounts of sulfur. In addition, the method of combining the sewage sludge with ashes is a favorable pro-ecological method of managing both fly ashes from the combustion of solid fuels and sewage sludge arising from wastewater treatment [16,17]. However, the composition of fly ash before sewage sludge stabilization for nature purposes should be carefully analyzed. It is also necessary to determine the heavy metals content in sewage sludge that is used in nature [18].

Considering the above, in order for fly ash from the combustion of solid fuels to be used for agricultural and natural purposes, their physical and chemical properties should be recognized in detail, so that they do not become a threat to individual components of the environment. The use of ashes as fertilizers is determined by many factors, including the content of nutrients as well as heavy metals toxic for the environment. In order for fly ash to be used for agricultural purposes, the content of nitrogen, phosphorus, potassium, and magnesium, that is, fertilizer components, as well as the content of hazardous substances such as metals: copper, zinc, cadmium, lead, nickel, chromium, should be tested [16]. It should be remembered that ashes from the biomass combustion can be characterized by the high ability of pollutants leaching and therefore their economic use can be limited. Many authors report that the content of water-soluble components in fly ash is high and can reach up to 61% [19–21] and even 70% [22].

Therefore, the purpose of the study was to assess pH and electrolytic conductivity of fly ashes from the combustion of solid fuels and to determine the amount of heavy metals leaching from water extracts of the ashes tested.

2. Material and methods

Fly ash samples for testing were collected in the region of north-eastern Poland, in the Podlaskie region, Choroszcz commune. The Choroszcz commune is influenced by the continental climate, which is characterized by long winters and short early spring [23,24].

Within the city, there is a municipal heating plant that provides thermal energy to housing estates and the hospital. Two types of boilers are installed: Eurobiomass Integra WH 3 with a capacity of 4,000 kW and Viessmann HW 200 with a capacity of 2,500 and 4,000 kW. However, the area of the Choroszcz commune is largely heated individually. Boilers, the medium of which is liquid gas or heating oil, are a minority [23]. Ten local heat sources from the city and commune of Choroszcz were selected for the study. Types of boilers and fuels used for their combusting are summarized in Table 1.

The research was conducted during three months: January, February, and March, during the heating season 2017/2018.

Ash samples were collected at specific measuring points in the period from January to March 2018. Five control points were selected, of which four were in the city of Choroszcz and one in the village of Żółtki. The location of measuring and control points was conditioned by the

Table 1 List of tested types of boilers and fuels

Measuring point	Boiler type	Fuel	Power boiler (kW)
1	Traditional boiler with an open combustion chamber	Wood, hard coal	17.5
2	Tiled stove	Wood	9
3	Hopper boiler with bottom combustion chamber	Hard coal	20.5
4	Automated charging boiler	Eco-pea coal	17
5	Hopper boiler with bottom combustion chamber	Wood, hard coal	21
6	Traditional boiler with an open combustion chamber	Wood, paper waste	28
7	Hopper boiler with an open combustion chamber	Eco-pea coal	19
8	Boiler with a gutter burner	Eco-pea coal	19
9	Chamber boiler with an upper combustion chamber	Pellet	19
10	Hopper boiler with bottom combustion chamber	Pellet	14

type of fuel combusted, the type of boiler, and the consent of the owner of the building where the heat source was located.

The first collection took place in early January. Subsequent ones were made in February and March 2018. During the sampling of material for testing, similar atmospheric conditions prevailed due to the season of the year at that time. Table 2 presents a description of the prevailing weather conditions.

Containers made of polyethylene with a total capacity of 135 cm³ were used to collect ash samples. The material from which they were made, did not change the chemical composition of collected material. Cooled ash for testing was collected with a blunt tool from the ash pan. Tightly closed and precisely described containers were transported to the Laboratory of the Department of Technology and Systems of Environmental Engineering at the Bialystok University of Technology. An experiment was conducted in which the leaching of heavy metals from aqueous ash solutions was determined as an indicator determining their suitability for agricultural purposes. The largest effort was made to investigate the content of individual elements in aqueous extracts from ashes. In addition, heavy metals were tested in the fly ash samples. Physicochemical tests of individual samples of aqueous extracts from ashes consisted of determining the content of individual elements by means of atomic absorption with flame atomization, specific electrolytic conductivity, and acidity. The first stage of determination was the preparation of samples. For this purpose, the test material was taken with a teaspoon and weighed 1 g on an electronic scale. Then 100 cm³ distilled water was measured using a measuring cylinder and transferred to the conical flasks.

Table 2

Parameters of prevailing weather conditions during sampling

After previous preparation, the test material was placed on an N-Biotek model (Korean) NB-205L shaker and shaken for 24 h. The next step was to filter the samples through quantitative filters. After previous preparation, the electrolytic conductivity was measured. The first step was to rinse the conductivity cell with distilled water. The vessel was then filled with the analyzed sample and brought to the temperature of 25°C. The subsequent step was to measure the concentration of individual elements in aqueous ash extracts after combusting the solid fuels by means of atomic absorption with flame atomization. For this purpose, the Thermo Scientific iCE3500 atomic absorption spectrophotometer (USA) with deuterium background correction was applied.

3. Results and discussion

In the fly ash samples, the content of selected heavy metals: Cr, Mn, Fe, Co, Ni, Cu, Zn, Pd, Cd was determined (Table 3). It was found that all ash samples were characterized by a high content of iron, manganese, and lead, regardless of the type of fuel burned. However, among the metals studied, the lowest concentrations were found for cobalt, chromium, and cadmium.

Based on laboratory analyses of aqueous extracts from fly ash, it was found that their selected physicochemical properties are characterized by seasonality (Table 4). The lowest value of pH, the contents of cadmium, cobalt, copper, chromium, and lead, were recorded for samples from the first collection – in January. However, during this period, increased content of iron, nickel, and zinc was found in aqueous extracts.

Parameter	Sampling						
	January (13.01.2018)	February (10.02.2018)	March (10.03.2018)				
Cloudy	Cloud cover	Cloud cover	-				
Temperature	–5°C	–7°C	2°C				
Wind	-	Weak	-				
Snowfall	-	-	-				

Table 3

Content of h	eavy metals	in the fly	ash samples
	/		

mg kg ⁻¹	1P	2P	3P	4P	5P	6P	7P	8P	9P	10P
Cr	3.05	0.94	5.01	4.52	6.18	2.05	7.26	4.43	3.95	2.67
Mn	115.20	22.73	30.89	34.97	83.72	613.44	46.24	18.81	1,575.73	534.25
Fe	1,793.84	149.22	2,129.88	1,891.48	3,270.56	654.72	2,286.06	1,942.93	239.21	481.44
Co	1.25	1.79	0.75	0.45	0.14	0.30	-	-	0.42	0.58
Ni	6.41	1.95	9.48	7.02	8.62	1.05	5.37	3.34	2.03	1.77
Cu	4.68	6.16	3.76	3.45	4.50	13.75	5.15	3.26	12.28	5.78
Zn	66.73	23.37	11.01	5.97	9.24	65.62	24.85	3.74	37.63	30.88
Pd	102.44	275.89	2.76	3.14	32.62	209.40	15.25	45.73	186.08	137.67
Cd	0.83	0.20	0.51	0.11	0.27	2.80	0.75	0.56	8.24	3.21

290

Season	Season		pН	Fe	Mn	Cd	Co	Cu	Ni	Cr	Zn	Pb
		$(\mu S \text{ cm}^{-1})$		(mg kg ⁻¹ DM)								
	Minimum	200.20	6.80	3.68	2.39	4.40	1.39	0.96	3.29	0.17	18.97	0.03
	Maximum	287.20	9.90	5.46	2.85	4.62	2.52	1.29	4.18	6.15	19.86	1.07
January	Average	238.39	8.58	4.64	2.61	4.52	1.91	1.17	3.81	3.09	19.48	0.57
	Median	228.70	8.50	4.64	2,59	4.53	1.86	1.22	3.87	3.46	19.50	0.59
	Standard deviation	30.58	_	0.57	0.15	0.08	0.37	0.11	0.31	1.69	0.31	0.32
	Minimum	202.00	8.20	3.08	2.26	4.48	1.67	1.03	2.84	0.66	17.69	0.85
	Maximum	352.40	9.90	5.04	2.50	4.65	2.65	1.34	4.37	3.75	19.92	1.61
February	Average	253.80	9.09	4.11	2.38	4.57	2.04	1.23	3.64	2.68	19.35	1.22
-	Median	244.55	9.00	4.11	2.40	4.60	1.94	1.25	3.70	2.81	19.72	1.17
	Standard deviation	50.58	_	0.57	0.08	0.06	0.28	0.09	0.41	0.90	0.79	0.24
	Minimum	204.00	7.90	3.29	2.16	4.46	1.73	1.21	3.23	1.70	15.48	1.10
	Maximum	282.50	10.5	4.94	10.31	4.66	2.69	1.36	4.10	6.36	19.86	2.20
March	Average	232.95	9.30	3.84	3.18	4.60	2.20	1.28	3.64	3.63	18.81	1.44
	Median	223.65	9.35	3.73	2.33	4.61	2.21	1.26	3.55	3.31	19.38	1.33
	Standard deviation	27.01	-	0.46	2.52	0.06	0.34	0.05	0.30	1.41	1.36	0.36
All season	Minimum	200.20	6.80	3.08	2.16	4.40	1.39	0.96	2.84	0.17	15.48	0.03
	Maximum	352.40	10.5	5.46	10.31	4.66	2.69	1.36	4.37	6.36	19.92	2.20
	Average	241.71	8.99	4.19	2.72	4.56	2.05	1.22	3.70	3.13	19.21	1.08
	Median	227.05	9.05	4.10	2.42	4.59	1.97	1.24	3.75	3.31	19.50	1.09
	Standard deviation	37.30	_	0.62	1.45	0.07	0.34	0.09	0.34	1.38	0.94	0.48

Table 4 Basic statistics of physicochemical properties of aqueous extracts of fly ash from biomass combustion

During the entire research period, the lowest pH value was recorded in January – it was equal to 6.8 in samples of water extracts from ashes collected from the 5th point of collection, which was fired with coal and wood. At this point, the local heat source was a hopper with a lower combustion chamber. The highest pH value of 10.5 was achieved in March in samples of water extracts from ashes from the 6th measuring and control point, where the heat source was a traditional boiler with an open combustion chamber fired with wood and paper waste (Fig. 1).

In terms of the reaction at particular sampling points, the highest result was obtained by the biomass-fired tiled stove throughout the entire research season with an average value of pH 10.0, and the lowest (pH 8.2) by the coal-fired boiler. According to [34], the type of fuel affects the ash acidity. They showed that biomass ashes are characterized by greater alkalinity compared to those from hard coal and lignite. The alkalinity of ashes is mainly due to potassium, sodium, magnesium, and calcium ions. Wood ashes have the most alkaline earth metals compared to ashes generated from hard coal and lignite. These metals occur in the form of oxides, for example, CaO, MgO [25,26].

Conductivity in the tested samples of aqueous fly ash extracts fluctuated significantly during the 3 research months. The minimum electrolytic conductivity equal to $200 \ \mu S \ cm^{-1}$ was achieved in February in water ash extracts from measuring point 5, the heat source of which was hopper with a bottom coal-fired combustion chamber. The maximum value was obtained in February in samples of aqueous extracts from fly ash from the 1st sampling point of

over 352 μ S cm⁻¹ in a building equipped with a traditional boiler with an open combustion chamber for wood and hard coal (Fig. 2).

Information on the content of inorganic compounds in aqueous solutions can be obtained based on the conductivity measurement [27]. Since biomass ash generally has a much higher content of such components as CaO, MgO, Na₂O, K_2O , P_2O_5 , the conductivity of aqueous extracts



Fig. 1. Changes in the pH of aqueous extracts of fly ash from the combustion of solid fuels from 10 measuring points.



Fig. 2. Changes in the electrolytic conductivity of water fly ash extract from solid fuel combustion from 10 measurement points.

of such ashes is higher compared to ash made from coal combustion [16].

To determine the leaching ability of heavy metals, the content of selected ions in aqueous ash solutions was examined. It was found that the total content of tested heavy metals was the highest in the case of zinc. The concentration of this metal in extraction solutions was about 19.0 mg kg⁻¹. This is confirmed by the fact that the metal in the form of a Zn²⁺ cation is extracted from ash only with the help of the aqueous solution. In addition, iron, cadmium, cobalt, manganese, copper, nickel, chromium, and lead ions were also present in the analyzed ashes, but the content of the latter was minimal, which confirms that this element is not subject to extraction from ash using water as the extractant. Based on the conducted tests, it was shown that leaching susceptibility of heavy metals from ash depends on the pH of an aqueous solution. In addition, many authors point out that the leaching ability of heavy metals from aqueous extracts prepared from fly ash from the combustion of solid fuels is affected by the pH of the solution [28-30]. Similar results were also obtained by [31], who proved that the concentration of heavy metals from industrial ashes from biomass

combustion depends on the pH of the aqueous solution and varies from 1 mg kg⁻¹ (Cu, Cd, Ni, Fe) up to 4–5 mg kg⁻¹ (Cr, Co) [31].

Based on the results obtained, it was found that the maximum iron content in aqueous ash extracts from the entire research period was 4.82 mg kg^{-1} DM. This value was found in ash samples from a wood-burning tiled stove. The lowest content of this element was found in ash extracts from a pellet-fired boiler (Fig. 3).

Manganese content was more than 5 mg kg⁻¹ DM in the ash samples from the 7th collection point, and 2.30 mg kg⁻¹ DM in ash samples from the 10th collection point (Fig. 3). This means that there were more than twice as many manganese ions in fly ash extracts from a coal and wood oven than in ash extracts obtained from a pellet stove.

Based on the results obtained, it was found that the concentration of cadmium in aqueous ash solutions ranged from 4.51 to 4.62 mg kg⁻¹ DM. Cadmium concentration in the tested extracts reached the lowest values in samples derived from the coal-fired boiler and the highest from the pellet-fired boiler (Fig. 3). The analysis of literature data on cadmium content confirms the fact that from the combustion of biomass alone, the cadmium content in ashes is higher than when co-firing 90% coal with 10% biomass [26]. Cobalt concentration in aqueous ash extracts varied at all measuring and control points. After analyzing the distribution of cobalt at individual sampling points for a period of 3 months, the highest result was recorded in aqueous ash extracts from an automated charging boiler (eco-pea coal) with an average value of 2.25 mg kg⁻¹ DM, and the lowest in aqueous ash extracts in the pellets-fired boiler (1.87 mg kg⁻¹ DM, Fig. 3). The copper content in the analyzed extracts also did not vary and ranged from 1.15 to 1.31 mg kg⁻¹ DM. The highest result was recorded in the extraction solutions from ashes from the coal-fired boiler, and the lowest in solutions from ashes from a wood-burning tiled stove and eco-pea coal boiler. According to research conducted by [26], the highest copper value was recorded in the case of biomass combustion, and the lowest in the co-combustion of biomass with coal, which was not reflected in its research.



Fig. 3. Content of tested heavy metals in aqueous extracts of fly ash.

After analyzing the distribution of nickel content throughout the entire research season at individual consumption points, the highest result was recorded in water ash extracts from the boiler No. 10 with an average value of 4.06 mg $kg^{\mbox{--}1}$ DM, and the lowest in the water ash extracts from the boiler No. 7 – 3.40 mg kg⁻¹ DM. In terms of nickel, the ash from hard coal combustion showed higher content than that from wood biomass combustion. Similar results were also obtained by [26] during the study of fly ash from biomass combustion and co-firing in fluidized bed boilers from the energy sector. The concentration of chromium in the research season in aqueous ash extracts fluctuated significantly. The highest content of chromium was noted in water ash extracts from a pellet-fired boiler: 4.39 mg kg⁻¹ DM, and the lowest: 1.40 mg kg⁻¹ DM, which occurred in water ash extracts from a tiled stove. Low lead concentration was found in the tested extracts. The content of this ion ranged from 0.75 to 1.54 mg kg⁻¹ DM. The highest concentration of lead ions was observed in extracts of ash originating from combusting pellets, and the lowest from wood with hard coal. Similar observations were presented by [26]. The minimum concentration of zinc occurred in aqueous ash extracts from the 2nd sampling point and amounted to 17.54 mg kg⁻¹ DM, while the highest was in the aqueous ash extracts from the 4th and 9th sampling points that were 19.80 mg kg⁻¹ DM. The highest values for zinc were obtained for boilers fired with eco-pea coal and pellets. Similar observations were made by other authors [32,33]. Comparing heavy metal content in ashes and aqueous extracts, it was found that cadmium and nickel had the highest percentage of leaching (which accounted for about 80% of leaching). In addition, cobalt, chromium, and zinc were more than 60% washed. In contrast, iron, manganese, and lead were washed away at around 1%.

To further detailed analyze the relationship between the physicochemical properties of water extracts of tested ashes, Pearson's linear correlation coefficients were calculated. Based on the calculated correlation coefficients, it was observed that there was a moderate relationship between seven indicators analyzed (Figs. 4 and 5). It was found that as the content of lead in ash water extracts increases, the content of cadmium and copper increases as well, while the content of iron decreases. In addition, a negative relationship was found between iron and cobalt content, and a positive relationship between cobalt and copper concentration (Fig. 4).

Tested extracts showed a moderate relationship at the level of r = -0.412 between acidity and zinc content. Therefore, the zinc content in the analyzed solutions increases as the pH value decreases (Fig. 5). However, the other pairs – pH-metal ions – showed a low relationship with the value of linear factor equal to about 0.2.

Over the three months, the analyzed water extracts from fly ash showed high variability in terms of physical and chemical properties from individual measuring and control points. Analyzing the results from selected power boilers, it was found that tested water extracts from ashes were characterized by high pH values, which confirms their alkaline character. The alkalinity of water extracts from ashes is mainly determined by the participation of calcium, potassium, sodium and magnesium metals, which may occur in the form of oxides, due to the significant proportion of oxygen in the elemental composition of fly ash. Water extracts of biomass ashes have much more alkaline earth metals (magnesium, calcium, potassium) compared to water extracts from hard coal and brown coal ashes [34].

The presence of calcium compounds in ash from brown coal combustion results from the presence of cellulose and related mineral compounds. The reaction of the analyzed extracts allows their use of light and acidic soils. Ash can successfully replace limestone and dolomite in regulating the soil pH. Studies by other authors showed that the addition of 1 kg of alkaline fly ash to the soil has the same effect on the acidity and calcium bioavailability as the addition of approximately 0.2 kg of pure CaCO₂ [35,36].

Electrolytic conductivity is an important property of aqueous fly ash extracts because it determines their suitability for the chosen method of use. A traditional boiler fired with mixed fuel (wood + hard coal) showed maximum conductivity among the other boilers. Conductivity indicates the content of mineral substances in aqueous extracts from fly ash [34].

Distribution of heavy metals in the tested samples varied; the highest content was found in water extracts from ashes derived from combustible material, which is coal. It can be unequivocally stated that furnace waste from hard coal and lignite contains a predominant amount of heavy metals than wood ashes. Similar results were also obtained by [34] comparing the physical properties of fly ash from coal, lignite, and biomass combustion. In their research, they proved that fly ash from biomass has a much lower content of metals (titanium, aluminum, iron) in their elemental composition than coal dust [34]. However, research conducted by [21,37] show that ashes from the combustion and co-firing of biomass may contain more components such as Ag, Au, B, Be, Ca, Cd, Cl, Cr, Cu, K, Mg, Mn, Na, Ni, P, Rb, Se, Zn, compared to ashes from coal combustion [21,37].

Based on a comparison of results obtained with the research conducted by [38], it was found that the use of tested ashes would allow for an increase in calcium and magnesium content. Due to this, the use of calcium fertilizers can be eliminated, reducing cultivation costs, and managing waste from the combustion of solid fuels. In addition, another positive aspect of the use of fly ash is the increase in the soil sorption complex, the degree of saturation, and the improvement of air-soil conditions. By comparing the results for ashes from coal combustion in boilers fired with eco-pea coal with the research of [36], the possibility of using these ashes for fertilizing purposes was proved. It is independent of the ash dose or crop species used. The use of fly ash from coal combustion causes an increase in the activity of enzymes that catalyze the transformation processes of soil organic matter.

In summary, it can be said that fly ash as a by-product is an interesting mineral additive that should be applied extensively in the industry. The direction of fly ash utilization depends on their physical properties, as well as chemical and mineralogical composition [13]. An analysis of the physicochemical properties of fly ash has shown that the alkaline nature of ash is associated with forms of heavy metals. Due to varying levels of occurrence, heavy metals contained in fly ash are present in forms that are difficult to



Fig. 4. Correlations between selected metal ions in water extracts of the ashes tested.

access and poorly soluble in water, or in the form of insoluble salts, which is why they are not absorbed by plants on alkaline soils. In this way, it can be determined what amounts of heavy metals can be washed away. In addition, ashes have valuable pozzolanic properties, which can have a beneficial effect on the immobilization of heavy metals to water-insoluble forms [26]. Based on the research, it was found that fly ash has the highest leaching ability in the case of heavy metal – zinc. The lead was an element that was not extracted from ash with water. Elements with a density greater than 5 g cm⁻³



Fig. 5. Correlations between the zinc content and the pH of the aqueous extracts of the ashes tested.

are almost completely not leached. Low leaching of heavy metals means that ashes can be used to bind elements found in the environment in excess amounts [16] and can be used for agricultural purposes.

4. Conclusions

- Method of combustion and type of fuel used had an impact on the content of heavy metals in aqueous fly ash extracts.
- Highest alkalinity was found in water extracts from ashes from wood combusting in a tiled stove, and the lowest when combusting the "eco-pea coal" in an automated hopper.
- The strongest correlation in tested ashes was noted between copper and iron.
- The greatest leaching ability from water extracts of ashes from various solid fuels was found in the case of zinc. However, lead was an element that was not extracted from ash with water.
- Alkaline reaction of water extracts has probably a large impact on the agricultural use of fly ash, the highest value of which was recorded in the fly ash water extract from a traditional boiler with an open combustion chamber fired with wood and paper.

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References

- R. Hela, M. Ťažký, Development of structural concrete with fly ash, Adv. Mater. Res., 1054 (2014) 143–147.
- [2] D. Rantung, S.W.M. Supit, S. Nicolaas, Effects of different size of fly ash as cement replacement on self-compacting concrete properties, Int. J. Sustainable Eng.: Proc. Ser., 1 (2019) 180–186.

- [3] S.M. Pathan, L.A.G. Aylmore, T.D. Colmer, Properties of several fly ash materials in relation to use as soil amendments, J. Environ. Qual., 32 (2003) 687–693.
- [4] M. Ahmaruzzaman, A review on the utilization of fly ash, Prog. Energy Combust. Sci., 36 (2010) 327–363.
- [5] R. Pires dos Santos, J. Martins, C. Gadelha, B. Cavada, A.V. Albertini, F. Arruda, M. Vasconcelos, E. Teixeira, F. Alves, J.L. Filho, V. Freire, Coal fly ash ceramics: preparation, characterization, and use in the hydrolysis of sucrose, Sci. World J., 2014 (2014) 7 pages, https://doi.org/10.1155/2014/154651.
- [6] Y. Luo, S. Zheng, S. Ma, C. Liu, X. Wang, Ceramic tiles derived from coal fly ash: preparation and mechanical characterization, Ceram. Int., 43 (2017) 11953–11966.
- [7] A. Satapathy, S.P. Sahu, D. Mishra, Development of protective coatings using fly ash premixed with metal powder on aluminium substrates, Waste Manage. Res., 28 (2009) 660–666.
- [8] A.A.B. Moghal, State-of-the-art review on the role of fly ashes in geotechnical and geoenvironmental applications, J. Mater. Civ. Eng., 29 (2017) 1–14.
- [9] A. Kaithwas, M. Prasad, A. Kulshreshtha, S. Verma, Industrial wastes derived solid adsorbents for CO₂ capture: a mini review, Chem. Eng. Res. Des., 90 (2012) 1632–1641.
- [10] A. Adamczuk, D. Kołodyńska, Equilibrium, thermodynamic and kinetic studies on removal of chromium, copper, zinc and arsenic from aqueous solutions onto fly ash coated by chitosan, Chem. Eng. J., 274 (2015) 200–212.
- [11] M. Wdowin, M. Franus, R. Panek, L. Badura, W. Franus, The conversion technology of fly ash into zeolites, Clean Technol. Environ. Policy, 16 (2014) 1217–1223.
- [12] K. Margeta, N.Z. Logar, M. Šiljeg, A. Farkas, Natural Zeolites in Water Treatment – How Effective is Their Use, Water Treatment, W. Elshorbagy, R.K. Chowdhury, Eds., Natural Zeolites in Water Treatment, Crotia, 2013, pp. 81–112.
 [13] M. Basu, M. Pande, P.B.S. Bhadoria, S.C. Mahapatra, Potential
- [13] M. Basu, M. Pande, P.B.S. Bhadoria, S.C. Mahapatra, Potential fly-ash utilization in agriculture: a global review, Prog. Nat. Sci.-Mater., 19 (2009) 1173–1186.
- [14] P. Kishor, A. Ghosh, D. Kumar, Use of fly ash in agriculture: a way to improve soil fertility and its productivity, Asian J. Agric. Res., 4 (2010) 1–14.
- [15] M. Piekarczyk, K. Kotwica, D. Jaskulski, The elemental composition of ash from straw and hay in the context of their agricultural utilization, Acta Sci. Pol. Agric., 10 (2011) 97–104.
- [16] M. Wójcik, F. Stachowicz, T. Trzepieciński, A.A. Masłoń, I. Opaliński, Possibility of recycling the biomass ashes in sewage sludge management, Arch. Environ. Prot., 44 (2018) 51–57.
- [17] C.D. Tsadilas, V. Samaras, P. Kazai, J. Sgouras, Fly Ash an Sewage Sludge Application on an Acid Soil and Their Influence on Some Soil Properties and Wheat Biomass Production, 12th ISCO Conference, Beijing, 2002.
- [18] J.Q. Xu, R.L. Yu, X.Y. Dong, G.R. Hu, X.S. Shang, Q. Wang, H.W. Li, Effects of municipal sewage sludge stabilized by fly ash on the growth of Manilagrass and transfer of heavy metals, J. Hazard. Mater., 217–218 (2012) 58–66.
- [19] S. Vassilev, D. Baxter, L. Andersen, C. Vassileva, An overview of the composition and application of biomass ash. Part 1 – phasemineral and chemical composition and classification, Fuel, 105 (2013) 40–76.
- [20] S. Vassilev, D. Baxter, L. Andersen, C. Vassileva, An overview of the composition and application of biomass ash. Part 2 potential utilization, technological and ecological advantages and challenges, Fuel, 105 (2013) 19–39.
 [21] S. Vassilev, C. Vassileva, D. Baxter, Trace element concentrations
- [21] S. Vassilev, C. Vassileva, D. Baxter, Trace element concentrations and associations in some biomass ashes, Fuel, 129 (2014) 292–313.
- [22] A.A. Bogush, J.A. Stegemanna, R. William, J.G. Wood, Element speciation in UK biomass power plant residues based on composition, mineralogy, microstructure and leaching, Fuel, 211 (2018) 712–725.
- [23] Study of Conditions and Directions of Spatial Development of the Town and Commune of Choroszcz, Choroszcz, 2017 (in Polish).
- [24] G. Borowski, M. Ozga, Comparison of the processing conditions and the properties of granules made from fly ash of lignite and coal, Waste Manage., 104 (2020) 192–197.

- [25] A. Fuller, J. Maier, E. Karampinis, J. Kalivodova, P. Grammelis, E. Kakaras, G. Scheffknecht, Fly ash formation and characteristics from (co-)combustion of an herbaceous biomass and a Greek lignite (low-rank coal) in a pulverized fuel pilot-scale test facility, Energies, 11 (2018) 1581.
- [26] G. Zając, J. Szyszlak-Bargłowicz, W. Gołębiowski, M. Szczepanik, Chemical characteristics of biomass ashes, Energies, 11 (2018) 2885.
- [27] O. Lahav, L. Birnhack, Aquatic Chemistry: For Water and Wastewater Treatment Applications, De Gruyter STEM, Germany, 2019.
- [28] Y. Zhang, B. Cetin, W.J. Likos, T.B. Edil, Impacts of pH on leaching potential of elements from MSW incineration fly ash, Fuel, 184 (2016) 815–825.
- [29] K. Huang, K.K. Inoue, H. Harada, H. Kawakita, K. Ohto, Leaching behavior of heavy metals with hydrochloric acid from fly ash generated in municipal waste incineration plants, Trans. Nonferrous Met. Soc. China, 21 (2011) 1422–1427.
- [30] W. Gwenzi, N.M. Mupatsi, Evaluation of heavy metal leaching from coal ash-versus conventional concrete monoliths and debris, Waste Manage., 49 (2016) 114–123.
- [31] J. Koniuszy-Nycz, Assessment of leaching and bioavailability of heavy metals in industrial ash from biomass, Sci. J., 167 (2018) 18–31 (in Polish).

- [32] P. Samaras, C.A. Papadimitriou, I. Haritou, A.I. Zouboulis, Investigation of sevage slude stabilization potential by the addition of fly ash and lime, J. Hazard. Mater., 154 (2008) 1052–1059.
- [33] E. Haustein, L. Grabarczyk, The impact of biomass co-firing with hard coal on selected physicochemical properties of fly ash, Energy Policy, t. 15, z. 2, (2012) 87–101 (in Polish).
- [34] A. Sobczyk, T. Czech, A. Jaworek, A. Krupa, Comparison of Physical Properties of Fly Ashes from Coal, Lignite and Biomass Combustion, Polish Academy of Sciences, Gdańsk, 2010, pp. 73–82 (in Polish).
- [35] H.T. Phung, H.V. Lam, A.L. Page, L.J. Lund, The practice of leaching boron and soluble salts from fly ash-amended soils, Water Air Soil Pollut., 12 (1979) 247–254.
- [36] D.K. Szponder, K. Trybalsk, Fly ash in agriculture modern applications of coal combustion by-products, TEKA Kom. Mot. Energ. Roln. – OL PAN, 11 (2011) 373–385.
- [37] S. Vassilev, D. Baxter, L. Andersen, C. Vassileva, An overview of the chemical com-position of biomass, Fuel, 89 (2010) 913–933.
- [38] E. Krzywy, C. Wołoszczyk, E. Możdżer, Possibility of producing granulated organic-mineral fertilizers from some municipal and industrial wastes, Chemik, 69 (2015) 684–697.