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# Trace elements and mineral composition of waste produced in the process of combustion of solid fuels in individual household furnaces in the Upper Silesian Industrial Region (Poland)

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#### ABSTRACT

This study presents preliminary research results, with regard to the concentration of chosen trace elements (Mn, Cr, Tl, Ni, Cu, Zn, As, Cd, Ba, Pb) in waste, which was produced in the process of combustion of solid fuels (hard coal and flotation concentrate of bituminous coal) in individual household furnaces in Poland (in the Upper Silesian Industrial Region). 27 samples of ash, 4 samples of hard coal and 2 samples of flotation concentrate of bituminous coal were prepared for the research. Methods such as: ICP-MS, X-ray diffraction by means of the powder method and scanning electron microscopy were used during the research. In the ash samples obtained from the combustion of hard coal, the highest average concentrations were: Mn (1477.7 ppm), Ba (1336.4 ppm) and Zn (599.7 ppm). In the samples obtained from the combustion of flotation concentrate of bituminous coal, the highest average concentrations was stated for: Zn (762.4 ppm), Mn (668.5 ppm), Pb (552.1 ppm) and Ba (211.7 ppm). Crystalline components were determined by used the X-ray diffraction method and the samples of ash obtained from the combustion of hard coal contained: anhydrite, gypsum, hematite, magnetite, quartz, calcite, mullite, periclase, kaolinite, dolomite, pyrite, sphalerite, galena and feldspars (albite–anorthite). The samples of ash obtained from the combustion of flotation concentrate of bituminous coal contain: pyrite, quartz, potassium feldspar, muscovite and kaolinite. The scanning electron microscope analysis enabled the identification of the chemical composition of single ash grains and determined their morphology (aluminosilicate forms, substance PbS and ZnS, oxides of Ni, Cu and Mn, monazite, xenotime).

KEY WORDS: ash, coal, chemical composition, mineral phases

## 1. Introduction

In the Polish power industry about 38 million tons of hard coal are burnt every year. The consumption of hard coal and hard coal silt for heating individual homes amounts to about 10 million tons per year (GUS, 2015). In individual household furnaces people in Poland very often use fuels, which are sulphated and poor in quality. Usually about 70% of waste in the form of ash and slag is thrown away in municipal waste dumps, and the is expelled with combustion gases through the chimney (GRODZIŃSKA-JURCZAK, 2001; DEN BOER ET AL., 2010). Domestic furnaces are characterized by low combustion temperatures (assessed to be around 270°C). Old solid fuel boilers, characterized by low thermal efficiency (45-70%) are still used very often.

In household furnaces flame coal and bituminous coal are fuels, which are used commonly. Flame coal can be used in all kinds of grate furnaces. It has high fly ash content (35-44%) and in praxis it does not agglomerate. Flotation concentrate bituminous coal maintains its hard coal properties (eg. chemical and mineral composition, carbon content, calorific value). It is a mixture of tiny coal grains and gangue, which along with it is carried away to special decanters during the process of mechanically working hard coal.

In individual households, chamber furnaces with a flat grate are usually used, because they are supplied manually and easily maintenaed. The respective phases of combustion (heating,

softening, degassing and swelling, ignition, combustion of the coke remains and its size reduction) are shifted in time (BURNLEY, 2007). Combustion in such furnaces is usually slower and lasts longer than in, for example, pulverizedfuel fired furnaces. The basic disadvantages of such solutions are: exploitation of installation of fuel supply, high fuel consumption, low thermal efficiency and lack of combustion gas dust extraction system. Moreover, usage of small coal size lowers furnace efficiency. Combustion of hard coal and flotation concentrate of bituminous coal contributes to air pollution, which is eight times higher in comparison to that from pulverized-fuel fired furnaces, which are used in big energetic buildings (Adhikari et al., 2014). Combustion conditions in individual household furnaces have substantial influence on chemical constitution and morphology of the ash grains obtained (KUTCHKO & KIM, 2006; WÓJCIK & SMOŁKA-DANIELOWSKA, 2008). Ash from individual domestic furnaces are potential sources of pollution not only into the atmosphere but also for the other components of the environment. Another factor is the necessity to dispose of solid waste, mainly as ash, on the communal waste dump.

In this paper, we report on the mineralogy and trace element geochemistry of ash generated in individual household furnaces in the Upper Silesian Industrial Region. The results show important implications for the highest values of enrichment coefficients of Cd, Pb, Zn and As in ash from flotation concentrate of bituminous coal.

# 2. Sampling

Material for research was collected in winter, during the heating season of 2011/2012 in the following cities: Rydułtowy, Orzesze and Piekary Ślaskie (Upper Silesian Industrial Region). In total, 33 samples were collected: 27 samples of ash (samples code A1 – A27), 4 samples of hard coal (samples code C1 – C4) and 2 samples of flotation concentrate of bituminous coal (samples code F1 - F2). Samples of ash were collected after combustion of hard coal (Rydułtowy, Piekary Slaskie) directly from the chamber, which was placed just under the grate furnace from two boilers (SWK-21 type) and from a boiler (S7WC-10 type), in which flotation concentrate of bituminous coal was combusted (Orzesze). All boilers were built of steel water frames. Their task is to heat water in central heating systems. The nominal thermal power for SWK-21 boilers 20 kW (Rydułtowy) and 24 kW (Piekary Śląskie), and for boiler S7WC-10 type 10 kW. Maximum permissible pressure for all types of boiler is 0.2 MPa. The temperature of water cannot be higher than  $95^{\circ}$ C (usually 60-90° C). The temperature of combustion gases in all types of boilers varies from 160 to 270°C.

The combustion of hard coal and flotation concentrate of bituminous coal in individual household furnaces lasted – without any breaks – two days. In order to clean each furnace after the first day of their work, the ashes have to be removed. Appropriate samples were taken after the second day of combustion, and was done regularly every two weeks. In every household furnace the usage of hard coal was about 40 kg/day, and hard coal silt 35 kg/day. 8 - 9 kilograms of ash was obtained daily From each furnace, in which hard coal was combusted, and from the combustion of flotation concentrate of bituminous coal about 6 kilograms of ash a day were obtained.

The hard coal, which was used in the combustion process was from the Rydułtowy Coal Mine and Mining Industry in Piekary Śląskie. The average content of ash was in the range of 4.2 – 12.6%. The fuel value equaled 28 – 30 MJ/kg. The flotation concentrate of bituminous coal samples were from the Knurów Coal Mine. Its fuel value equaled 17 MJ/kg, and ash content 25%.

# 3. Methodology

The content of trace elements (Mn, Cr, Tl, Ni, Cu, Zn, As, Cd, Ba, Pb) has been analysed at Activation Laboratories (Canada), by means of atomic emission spectroscopy ICP-MS (Jarrell Ash model Enviro and a Perkin Elmer model 6000). Activation Laboratories Ltd. Canada performs analyses for trace elements by dissolving sample in solutions consisted of 10 ml of HCl –  $HNO_3$  – HClO<sub>4</sub> – HF at 200°C, diluted to 10 ml in aqua regia.

Morphological analyses have been performed using the analytical scanning electron microscopy method with a JEOL JSM-5410 scanning electron microscope equipped with EDS with a NORAN Vantage microanalytical system (Laboratory of Scanning Microscopy, Jagiellonian University in Cracow). The beam increasing voltage equalled 15–25 kV, intensity of 20 nA. Analyses using by Analytical Scanning Elektron Microscopy (ASEM) were made using a scanning electron microscope produced by PHILIPS XL 30 equipped with EDS attachment. The voltage was 15 kV, and bundle intensity of 20 nA. Analyses were made in the Laboratory of Scanning Microscopy at the Faculty of Earth Sciences of the University of Silesia on the polished sections. Hard coal and flotation concentrate of bituminous coal ashes samples were sealed in epoxy resin and polished with diamond paste.

The mineral composition was analyzed by Xray diffraction (XRD) method applying a Philips PW 3710 diffractometer, utilizing CuKa1 radiation with a graphite monochromator. The lamp electric voltage was 50 KV with current intensity of 30 mA. Impulse time counting was 3 seconds and the rate of tape movement was 0.02° per minute.

# 4. Research results and discussion

#### 4.1. Mineralogy

The main crystalline elements which were marked by means of X-ray diffraction in the ash samples obtained from hard coal combustion (samples A10 – 27) were: quartz, anhydrite, hematite, magnetite, calcite, mullite, goethite, periclase, kaolinite, sphalerite, galena and feldspars (albite - anorthite). The estimated participation of coal matter in the investigated samples of ash amounted to 41.3% to 48.5% vol.%. The coal matter contentand rated value, was estimated by the use of the Rietveld method and X'Pert computer programme. Quartz, muscovite, kaolinite, calcite and anhidrite were identified in the hard coal samples (C1 - C4), while quartz (12.2 - 22.8 vol.%) and kaolinite (9.7 – 11.3 vol.%) predominated. In considerable amounts of pyrite were also identified (3 - 4% vol.%).

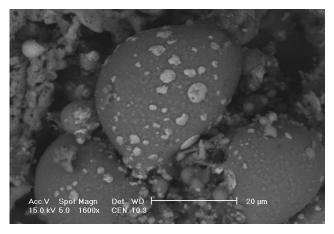
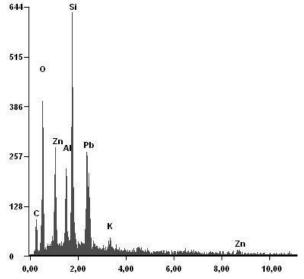


Fig. 1. SEM image and EDS spectrum of aluminosilicate particle in ash from hard coal combustion in individual household furnaces

The next group consisted of sulphides of lead, zinc and iron. The substance PbS was in the investigated samples in the form of sharp-edged forms, which had a smooth surface and were not bigger than 3  $\mu$ m (Fig. 2a). The substance ZnS was represented

In the samples of ash obtained from the flotation concentrate of bituminous coal combustion (samples A1 – A9) pyrite, quartz, potassium feldspar, muscovite and kaolinite were identified. The X-ray structure analysis of investigated samples indicated a very high pyrite content (about 10% of the total volume). The coal matter content, amounted to between 61.4% to76.3%. Pyrite was identified in the samples of coal silt from Orzesze (F1 - F2) and amounted to 11%. Moreover quartz, muscovite/illites, kaolinite, dolomite, calcite and albite were identified. Many researchers identified similar (kaolinite, pyrite, quartz, calcite, siderite, galena, feldspars, boehmite) minerals in coal (WARD, 1977, 2002; GOODARZI ET AL., 1985; VASSILEV & VASSILEVA, 1998; HOWER ET AL., 2001; LI ET AL., 2001).

The examination by means of a scanning electron microscope enabled identification of the chemical composition of single ash grains and determined their morphology. The ash obtained from hard coal combustion had mainly aluminosilicate forms with smooth surfaces and spherical shapes. The sizes of aluminosilicate spheres were between 5  $\mu$ m to 600  $\mu$ m, and the following elements were adsorbed on their surface: calcium, potassium, magnesium, iron, barium and titanium. Aluminiosilicate substance, which had irregular forms, and aporous surface and measured up to 100  $\mu$ m. Aluminosilicate particles, containing iron, lead, zinc or manganese could often be found in cokes (Fig. 1).



probably by sphalerite, which built units and their size was about 5  $\mu$ m. In the ash one could also notice single grains of pyrite, which built longitudinal forms (length about 600  $\mu$ m) and aggregate concentrations, of the sizes ranged 30 to 250  $\mu$ m,

were observed. In the samples of ash obtained from hard coal combustion numerous sulphates represented by barite and gypsum were noticed. Barite grains had different forms – both massive and dense, as well as openwork. Their size did not exceed 15  $\mu$ m. Gypsum grains had mostly secondary nature. One rarely noticed crystals, where present they were in the twin form ("swallow tails"). In investigated ash samples concentrations contained iron oxides were observed. They build oval, spherical, feathery and tabular forms and their size did not exceed 20  $\mu$ m. Bigger grains (100-120  $\mu$ m) were in the form of aggregates. There were also oxide forms, which contained Ni, Cu and Mn (Fig. 3b).

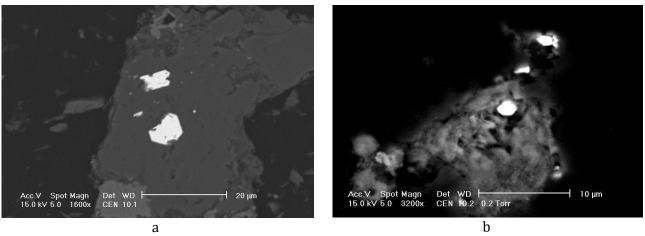


Fig. 2. SEM image of PbS particles (very bright particles) in ashes from hard coal (a) and flotation concentrate of bituminous coal (b) combustion in individual household furnaces

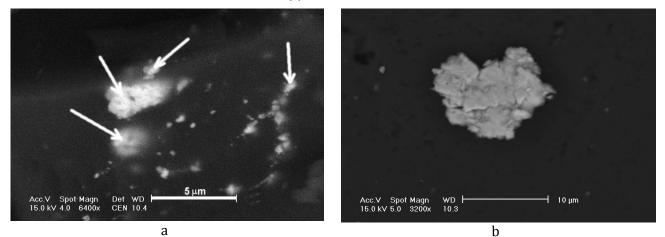


Fig. 3. SEM image oxides forms of Ni, Cu and Mn (very bright particles) in ashes from flotation concentrate of bituminous coal (a) and hard coal (b) combustion in individual household furnaces

In the ash samples obtained from hard coal combustion one could find: phosphate of rare earth elements represented mainly by cerium monazite. The sizes of these grains were small (maximum 10  $\mu$ m) and very often had traces of dissolution (Fig. 4a). Additionally, grains of xenotime, which size did not exceed 2  $\mu$ m, were identified.

In the samples of ash obtained from flotation concentrate of bituminous coal combustion one could identify substances which consisted of uncombusted parts of hard coal silt. Aluminosilicate could be found in the form of big, irregular, porous forms, with sizes from 200 to 500  $\mu$ m. The following

elements were adsorbed on its surface: Ba, Fe, Mn, Ni, Zn, Pb, Ca, K and Mg.

Barite grains marked in the samples of ash obtained from hard coal silt combustion were smaller (up to 10  $\mu$ m) than those, which were marked in the ash samples from hard coal combustion. They built massive and dense forms and had smooth surfaces.

In the investigated samples of ashes observe grains of pyrite and chalkopyrite were observed very often (Fig. 5). There were more grains of pyrite, than of chalcopyrite and they were relatively small (10  $\mu$ m). They built massive, irregular forms. Usually chalcopyrite coexisted with pyrite.

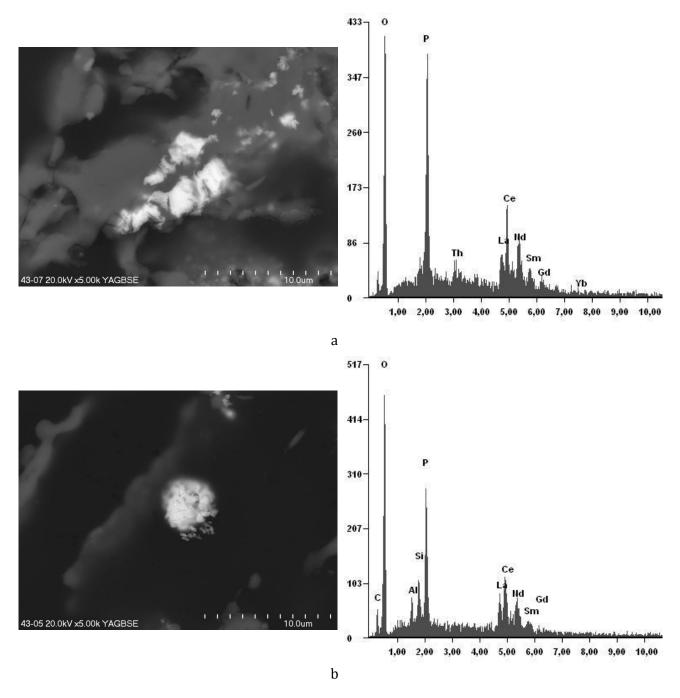


Fig. 4. SEM image and EDS spectrum of monazite in ashes from hard coal (a) and flotation concentrate of bituminous coal (b) combustion in individual household furnace

In all the samples investigated from the flotation concentrate of bituminous coal combustion monazite and xenotime grains were observed. Monazite grains had smooth surfaces, were dense and their size was between 2 to 50  $\mu$ m (Fig. 4b). Not all observed monazite grains contained radioactive thorium. Xenotime grain size did not exceed 3  $\mu$ m.

In the investigated samples obtained from the flotation concentrate of bituminous coal combustion oxide forms of iron were rarely observed. They mostly built aggregates and their size was between 20 to several dozen micrometers. What is more, grains built of "heavy metal" oxides (Ni, Cu and Mn) were found (Fig. 3a).

The main components of ash from power plants as well as from household furnaces are diverse particles of glaze, which contain: aluminium, silicon, iron, calcium, sodium, titanium. The ash, which is obtained in the process of combustion of solid fuels in individual household furnaces, contains amongst others: pyrite, which is also present in hard coal and flotation concentrate of bituminous coal. There are also phases of different morphology, which contain iron oxides. The low temperature of combustion also causes the creation of artificial phases and it is very difficult to mark them. In all the ash samples of the ashes there were observed so called cokes (amorphous type of coal). The size of cokes was measured exactly and was between several to several dozen micrometres.

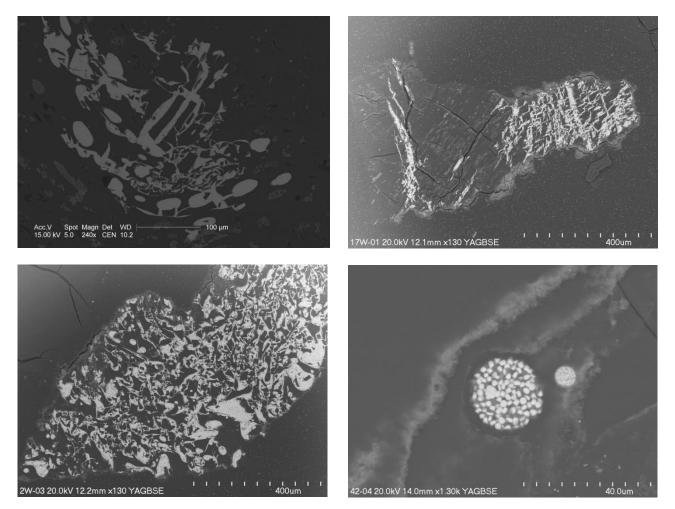


Fig. 5. SEM image o f pyrite forms in ash from flotation concentrate of bituminous coal combustion in individual household furnaces

## 4.2. Chemical composition

The results of the concentrations of the chosen trace elements of analyzed samples are presented in Table 1. In the samples of ash, which were obtained from hard coal combustion (samples A10 – A27) the highest average concentration was measured for Mn – 1477.7 ppm (min. 684 ppm, max. 1691 ppm), Ba – 1336.4 ppm (min. 1050 ppm, max. 2360 ppm), and Zn 599.7 ppm (min. 372 ppm, max. 673 ppm).

In the samples investigated there was an average concentration of Ni equal to 122.5 ppm (min. 39 ppm, max. 148 ppm), Pb – 75.9 ppm (min. 30 ppm, max. 97 ppm), Cu – 110.9 ppm (min. 97 ppm, max. 133 ppm), and Cr – 100.5 ppm (min. 30 ppm, max. 126 ppm). The average concentration of Tl

and Cd in the samples of hard coal ash equaled 0.5 ppm and 0.9 ppm respectively. The marked concentration of As in the investigated samples was in the range: 10.2 – 28 ppm (on average 21.4 ppm).

In ash samples, which were obtained from the flotation concentrate of bituminous coal combustion (samples A1 – A9) the highest average concentration was measured for Zn – 762.4 ppm (min. 119 ppm, max. 1460 ppm), Mn – 668.5 ppm (min. 420 ppm, max. 991 ppm), Pb – 522.1 ppm (min. 231 ppm, max. 766 ppm) and Ba – 211.7 ppm (min. 125 ppm, max. 367 ppm). The average concentration of Pb, which was measured in these samples was much higher than in the ash samples which were obtained from hard coal combustion.

Samples	Mn	Cr	Tl	Ni	Cu	Zn	As	Cd	Ba	Pb
F1 – F2	83.0	6.5	-	11.6	20.1	30.0	3.0	0.1	228.0	15.5
	81.0	6.1	-	10.8	19.6	32.0	2.8	0.1	226.0	17.0
Average	82.0	6.3	-	11.2	19.8	31.0	2.9	0.1	227.0	16.2
A1 - A9	986.0	132.0	2.3	102.0	198.0	1190.0	102.0	13.0	170.5	749.0
	429.0	87.0	0.2	53.0	64.0	149.0	22.0	0.2	125.0	281.0
	738.0	128.0	3.3	111.0	206.0	1460.0	100.0	9.6	196.0	672.0
	420.0	96.0	0.2	59.0	70.0	138.0	15.0	0.1	367.0	231.0
	991.0	141.0	2.1	101.0	186.0	1230.0	98.0	11.0	173.0	766.0
	431.0	88.0	0.1	52.0	54.0	151.0	21.0	0.2	261.0	293.0
	796.0	131.0	2.8	108.0	195.0	1200.0	101.0	10.5	176.0	692.0
	418.0	82.0	0.2	51.0	49.0	146.0	22.0	0.4	256.0	270.0
	808.0	126.0	3.2	111.0	188.0	1198.0	104.0	1.1	181.0	745.0
Average	668.5	112.3	1.6	83.1	134.4	762.4	65.0	5.1	211.7	522.1
Enrichment	8.2	17.8	1.6	4.2	6.8	24.6	22.4	51.0	0.9	32.2
A1-9/F1-2										
C1 – C4	128.0	74.0	0.02	35.0	184.0	37.0	4.2	0.5	410.0	63.0
	131.0	71.0	-	32.0	172.0	36.0	3.9	0.5	470.0	59.0
	196.0	74.0	0.07	23.0	73.0	75.0	1.1	0.5	460.0	45.0
	171.0	54.0	0.02	28.0	64.0	69.0	0.8	0.1	338.0	44.0
Average	156.5	68.2	0.04	29.5	123.2	54.2	2.5	0.4	419.5	52.7
A10 – A27	1610.0	112.0	0.64	143.0	117.0	662.0	26.6	1.7	1260.0	97.0
	1691.0	132.0	0.84	148.0	118.0	620.0	27.4	0.7	1560.0	48.0
	684.0	30.0	0.52	39.0	123.0	372.0	10.2	-	1450.0	30.0
	1640.0	108.0	0.71	139.0	112.0	631.0	25.1	0.8	1180.0	96.0
	1560.0	101.0	0.52	141.0	114.0	625.0	18.6	1.4	1180.0	88.0
	1630.0	109.0	0.58	141.0	108.0	655.0	24.5	1.3	1190.0	89.0
	1340.0	78.0	0.07	56.0	118.0	630.0	11.4	0.5	2360.0	46.0
	1680.0	126.0	0.90	151.0	121.0	636.0	28.0	0.8	1490.0	84.0
	1620.0	110.0	0.68	148.0	120.0	673.0	25.4	1.4	1230.0	86.0
	1590.0	108.0	0.56	139.0	114.0	412.0	26.1	0.8	1230.0	92.0
	1590.0	98.0	0.62	112.0	101.0	592.0	18.4	0.4	1160.0	88.0
	1520.0	101.0	0.59	131.0	106.0	601.0	21.5	1.2	1490.0	72.0
	1230.0	102.0	0.51	111.0	100.0	621.0	19.0	1.2	1320.0	66.0
	1498.0	100.0	0.21	126.0	97.0	641.0	21.6	0.2	1400.0	71.0
	1506.0	97.0	0.46	136.0	111.0	606.0	19.3	0.4	1110.0	83.0
	1380.0	91.0	0.11	115.0	103.0	596.0	20.6	0.9	1200.0	76.0
	1410.0	106.0	0.20	109.0	106.0	580.0	22.0	0.6	1196.0	69.0
	1420.0	101.0	0.36	120.0	108.0	641.0	19.8	1.1	1050.0	85.0
Average	1477.7	100.5	0.5	122.5	110.9	599.7	21.4	0.9	1336.4	75.9
Enrichment	9.4	1.5	12.5	4.1	0.9	11.1	8.6	2.2	3.2	1.4
A10-27/C1-4										

Table. 1. Trace elements (ppm) of ashes produced in the process of combustion of solid fuels in individual household furnaces in Poland

In the ash samples of flotation concentrate of bituminous coal an average concentration of Cd was 5.1 ppm, and Tl – 1.6 ppm. The average concentration of As was 65 ppm, and Cu 134.4 ppm. These values are higher in comparison with the ash samples, which were obtained from the combustion of hard coal.

Cadmium in the ash samples fromflotation concentrate of bituminous coal is 5.1 ppm compared with 0.1 ppm in the flotation concentrate of bituminous coal. As such all the trace elements are enriched in the ash samples of flotation concentrate of bituminous coal compared with hard coal, whereas Tl and Ba are enriched in ash from hard coal. Cadmium, Pb, Zn and As were highly enriched in ash from flotation concentrate of bituminous coal (EF > 20) when compared with the flotation concentrate of bituminous coal. Thallium in the samples of flotation concentrate of bituminous coal and hard coal are BDL (below the detection limit) compared with 0.5 - 1.6 ppm in ash (Table 1). Higher concentrations of elements in the ash samples which were obtained from flotation concentrate of bituminous coal are attributed to the finer particles (QUEROL ET AL., 2009; RACLAVSKA ET AL., 2009; VERMA ET AL., 2015). The enrichment pattern in ash samples of flotation concentrate of bituminous coal were as follows as: Cd >Pb> Zn > As > Cr >Mn> Cu > Ni > Tl > Ba; in ash hard coal samples: Tl > Zn >Mn>As > Ni > Ba > Cd > Cr > Pb > Cu.

The hards coal which was combusted in house furnaces in Piekary Śląskie is also used by the Municipal Heat Supply Company. A heat plant with an installed capacity of 80.5 MW, is equipped with a system for fume gases dedusting multicyclone type (dedusting efficiency at the level of 70%). The temperature in the combustion chamber does not exceed 800°C. In the samples of ash from the heat plant in Piekary Slaskie average values of concentrations of Ba (277 ppm) and Mn (762 ppm) were measured (own unpublished research) and are convergent with values from the samples of ash from the individual house furnaces. Average values of Cu (230 ppm), Cr (204 ppm), Zn (1215 ppm), Pb (815 ppm), Ni (163 ppm), As (105 ppm), Tl (10.6 ppm) and Cd (11.5 ppm) concentrations are higher in comparison with concentration values of these elements in samples of ash from individual house furnaces.

### 4.2.1. Hard coal

In the investigated samples of hard coal the average values of trace elements amount to: Ba (419.5 ppm), Mn (156.5 ppm), Cu (123.2

ppm), Cr (68.2 ppm), Zn (54.2 ppm), Pb (52.7 ppm) and Ni (29.5 ppm). They are higher in comparison to average values of these elements contained in the Polish hard coal: Ba (116 ppm), Mn (ppm), Cu (17 – 30 ppm), Cr (ppm), Zn (20 – 48 ppm), Pb (20 – 40 ppm) and Ni (10 – 56 ppm) (KABATA-PENDIAS & SZTEKE, 2012). The content of analyzed trace elements in the investigated hard coal samples is similar to the world's hard coals: Ba (20 – 1000 ppm), Mn (5 – 300 ppm), Cu (0.5 – 50 ppm), Cr (0.5 – 50 ppm), Zn (5 – 300 ppm), Pb (2 – 80 ppm) i Ni (0.5 – 50 ppm (SWAINE, 1990; DAI ET AL., 2006).

#### 4.2.2. Flotation concentrate of bituminous coal

In the investigated samples of flotation bituminous concentrate of coal average concentration values of elements amount to: Ba (227 ppm), Mn (82 ppm), Cu (19.8 ppm), Pb (16.2 ppm), Cr (6.3 ppm), Zn (31 ppm) and Ni (11.2 ppm). On the basis of the literature (LUTYŃSKI & SZPYRKA, 2003; BAIC ET AL., 2012; DZIENGIELEWSKA, 2014) average values of concentrations of these elements in Polish flotation concentrate of bituminous coal are higher, or at a similar level: Ba (423.91 - 708.11 ppm), Mn (288 - 5693.28 ppm), Cu (5.54 – 7.78 ppm), Cr (<0.004 – 5.57 ppm), Zn (89.91 – 326 ppm), Pb (19.58 – 48 ppm) and Ni (10.61 – 30 ppm).

### 5. Conclusions

Samples of ash from the process of flotation concentrate of bituminous coal combustion are characteristic for their high concentration of Pb (522.1 ppm), Cd (5.1 ppm), As (65 ppm) and Zn (762.4 ppm). In the process of low temperature combustion the ash from the coal silt does not undergo substantial enrichment in Cd (EF > 50), Pb (EF > 30), Zn and As (EF > 20) in comparison to ash from hard coal. The ash from hard coal is enriched in Tl and Zn (EF > 10) and As (EF > 8). Samples of ash from the process of hard coal combustion have the highest concentrations of Mn and Ba. All samples of ash irrespective of the kind of combusted fuel are enriched in Mn (EF > 8) and Ni (EF > 4).

Generally, the samples of ash are different as far as the content of the coal matter and fineness are concerned, what can cause higher values of Pb, As, Cd and Tl concentrations in the ashes from the flotation concentrate of bituminous coal. The ash from the hard coal produced in individual house furnaces contains a lower content of Cu, Cr, Zn, Pb, Ni, As, Tl and Cd, than the ash from the heat plant. It is mainly caused by different technology of the coal combustion process and its fineness.

In the ash samples obtained from the flotation concentrate of bituminous coal combustion and hard coal combustion substantial amounts of pyrite was identified. Quartz, muscovite/illites, kaolinite, dolomite, calcite and albite were also identified in the investigated samples. The mineralogical composition of ashes coming from the combustion of hard coal and in the flotation concentrate of bituminous coal in the domestic individual furnaces is similar. Analyses which were conducted by means of scanning electron microscopy indicated that on the ash samples dominate the coal matter and aluminosilicate glassy phases. In all the samples investigated from the flotation concentrate of bituminous coal combustion monazite and xenotime were identified. Monazite containing thorium was more frequently observed in the samples of ash produced from the hard coal.

The results obtained for the chemical – mineralogical research of the ash from household furnaces suggest the need to continuation, mainly because of their content of toxic elements and their further migration into the environment.

#### References

- Adhikari B., Dahal K.R., Khanal S.N. 2014. A review of factor affecting the composition of municipal solid waste landfill leachate. *Int. J. Eng. Sci. Innov. Tech.*, 3 (5): 272-281.
- Baic I., Witkowska Kita B., Lutyński A., Suponik T. 2012. Parametry chemiczne depozytów mułów węglowych. Baza danych DMW. *Polit. Energetyczna*, 15, 3: 235-242.
- Burnley SJ. 2007. A review of municipale solid waste composition in the United Kingtom. *Waste Manage.*, 27 (10): 1274-1285.
- Dai S.F., Ren D.Y., Chou C.L., Li S.S., Jiang Y.F. 2006. Mineralogy and geochemistry of the No. 6 Coal (Pensylvanian) in the Janger Coalfield, Ordos Basin, China. *Int. J. Coal Geol.*, 66: 253-270.
- Den Boer E., Jędrczak A., Kowalski Z., Kulczycka J., Szpadt R. 2010. A review of municipal solid waste composition and quantities in Poland. *Waste Manage.*, 30: 369-377.
- Dziengielewska M. 2014. Charakterystyka mineralogiczna oraz skład chemiczny mułów węglowych. Praca magisterska. Uniw. Śląski: 61.

- Goodarzi F., Foscolos A.E., Cameron A.E. 1985. Mineral matter and elemental concentrations in selected western Canadian coals. *Fuel*, 64: 599-605.
- Grodzińska-Jurczak M. 2001. Management of industrial and municipal solid wastes in Poland. Resources, *Conserv. Recycling*, 32: 85-103.
- GUS: Główny Urząd Statystyczny 2015. Zużycie paliw i nośników energii w 2014 r., Warszawa 2015 (http://stat.gov.pl/ obszary-tematyczne/srodowisko-energia/energia/zuzyciepaliw-i-nosnikow-energii-w-2014-r-,6,9.html).
- Hower J.C., Williams D.A., Eble C.F., Sakulpitakphon T., Moecher D.P. 2001. Brecciated and mineralized coals in Union Country, Western Kentucky coal field. *Int. J. Coal Geol.*, 47: 223-234.
- Kabata-Pendias A., Szteke B. 2012. *Pierwiastki śladowe w* geo- i biosferze. Wyd. IUNG-BIP, Puławy.
- Kutchko B.G., Kim A.G. 2006. Fly ash characterization by SEM-EDS. *Fuel*, 85: 2537-2544.
- Li Z., Moore T.A., Weaver S.D., Finkelman R.B. 2001. Crocoite: an unusual mode of occurrence for lead in coal. *Int. J. Coal Geol.*, 45: 289-293.
- Lutyński A., Szpyrka J. 2003. analiza jakosci mułów węgla kamiennego zdeponowanych w osadnikach ziemnych. *Górn. Geol.*, .6, 2: 121-123.
- Querol X., Fernández-Turiel J.L., Lopez-Soler A. 2009. Trace elements in coal and their behaviour during combustion in a large power station. *Fuel*, 74(3): 331–343.
- Raclavska H., Raclavsky K., Matysek D. 2009. Colour measurement as a proxy method for estimation of changes in phase and chemical composition of fly ash formed by combustion of coal. *Fuel*, 88: 2247–54.
- Swaine D.J. 1990. Trace Elements in Coal. Butterworths, London.
- Vassilev S.V., Vassileva C.G. 1998. Comparative chemical and mineral characterization of some Bulgarian coals. *Fuel Proc. Tech.*, 55: 55-69.
- Verma S.K., Masto R.E., Gautam S., Choudhury D.P., Ram L.C., Maiti S.K., Maity S.K. 2015. Investigations on PAHs and trace elements in coal and its combustion residues from a power plant. *Fuel*, 162: 138-147.
- Ward C.R. 1977. Mineral matter in the Harrisburg-Springfield (No. 5) coal member of the Carbondale Formation, Illinois Basin. *Illinois State Geol. Surv., Circular*, 498, 35.
- Ward C.R. 2002. Analysis and significance of mineral matter in coal seams. *Int. J. Coal Geol.*, 50: 135-168.
- Wójcik M., Smołka-Danielowska D. 2008. Phase minerals composition of wastes formed In bituminous coal combustion from individual domestic furnace in the Piekary Śląskie town (Poland). *Polish J. Environ. Stud.*, 17 (5): 817-821.
- https://rewolucjaenergetyczna.wordpress.com/2015/03/0 2/ogrzewanie-i-palenie-w-piecu-podstawy/