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Analysis of the content of nickel, chromium, lead and zinc in solid products of coal combustion (CCPs) coming from Polish power plants

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Abstract. According to data from the European Environmental Agency (EEA), taking into account only the energy production and distribution sector, Poland emits almost 12.4% of chromium, 13.6% of nickel, 23.5% of lead and 28.9% of zinc annually when compared to the total emissions of these pollutants released by the EU Members (EU28) in this sector [1]. Coal combustion processes constitute one of the biggest emission sources of the above-mentioned elements into the environment. According to data found in the literature of the subject, the amounts of Cr, Ni, Pb and Zn in Polish hard coals from the Upper Silesian Coal Basin are 7.3, 9.8, 24.3 and 53.6 mg/kg, respectively [2]. During coal combustion these elements are mostly accumulated in bottom and fly ash. However, a large part of them is released into the atmosphere in the form of gases or particles associated with fly ash [3]. Identification of distribution of the above-mentioned elements between by-products from the coal combustion processes (CCPs) is necessary to develop effective methods of reducing the emission of these elements into the environment. In the article the content was determined of four ecotoxic elements (Cr, Ni, Pb and Zn) in coal blends, samples of fly ashes, ash-slag samples and products of desulphurization (gypsum and filter cakes) which came from two Polish fossil fuel power plants. The content of the elements in all samples was determined with the application of Atomic Absorption Spectrometry with Flame Atomization (FAAS).

1. Introduction

Coal, as a sedimentary rock of organic origin, in addition to the major elements (C, H, O, N), also contains relatively large amounts of ecotoxic elements which negatively affect the environment and the human body. Chromium, nickel, lead and zinc are among the most harmful ones in this aspect. In the foreign hard coals, the contents of these elements are: $17.0 \pm 1.0 \text{ mg}_{\text{Cr}}/\text{kg}$, $17.0 \pm 1.0 \text{ mg}_{\text{Ni}}/\text{kg}$, $9.0 \pm 0.7 \text{ mg}_{\text{Pb}}/\text{kg}$ $28.0 \pm 2.0 \text{ mg}_{\text{Zn}}/\text{kg}$ [4]. In contrast, Polish hard coals derived from the Upper Silesian Coal Basin are characterised by lower contents of chromium and nickel ($7.3 \text{ mg}_{\text{Cr}}/\text{kg}$ and $9.8 \text{ mg}_{\text{Ni}}/\text{kg}$). On the other hand, the lead and zinc values are respectively 24.3 and 53.6 mg/kg, which is about 2 times higher than their world average content in hard coal [2].

Annual coal consumption in Poland exceeds 70 million tonnes, out of which almost 60% belongs to the energy sector [5]. During the combustion of coal, apart from the emission of sulphur and nitrogen oxides, numerous ecotoxic elements are also released. According to the data of the European



Environment Agency (EEA), considering only the areas of production and distribution of energy, Poland annually emits 12.4% of chromium, 13.6% of nickel, 23.5% of lead and 28.95% of zinc in relation to the total emissions of these pollutants released in the energy sector by the Member States of the EU28, which classifies Poland as one of the biggest emitters of these elements into the environment [1].

The scale of ecotoxic elements emissions depends on the quantity and quality of solid fuels consumed in the combustion process, conditions in the boiler and the flue gas installations (installations for the removal of nitrogen oxides, sulphur oxides and particles, as well as fly ash) [6-10]. According to Zhao et al. [9] the use of Electrostatic Precipitators (ESP), and a wet flue gas desulfurization installation (WFGD) in combination with Wet Electrostatic Precipitators (WESP) allows for additional cleanup of the flue gas from the ecotoxic elements (ecotoxic elements content in the flue gas emitted to the environment, in this case, amounted to $0.00\text{--}1.33\text{ }\mu\text{g}/\text{m}^3$). In addition, the presence of small amounts of Ni, Cr, Zn, and Pb was recorded in gypsum, while much larger quantities of those elements were registered in the waste waters from WFGD.

In coal, elements such as Cr, Ni and Pb are associated mostly with clay minerals. Pyrite and other sulphites are related to Zn, Ni and Pb presence [3, 7, 8]. During the combustion processes, these elements enter the gaseous form and then mostly accumulate in the bottom ashes (slag) and the fly ashes that are efficiently separated from the flue gas on an ESP [11]. Despite this, the smallest particles of fly ash escape to the atmosphere. In the literature [7,8 12-14], a widely described correlation can be found between the content of the above-mentioned ecotoxic elements and the size of fly ash particles. These studies confirm that with a decrease of the particle size of fly ash, the harmful elements content increases. Especially enriched in these elements are particles below $2.5\text{ }\mu\text{m}$, which are also the most dangerous ones to the human body. In 1990 the U.S. Environmental Protection Agency (US EPA) published a list of hazardous air pollutants (HAPs) that negatively affect the human health including Ni, Cr and Pb. Furthermore, according to the International Agency for Research on Cancer, chrome and nickel have carcinogenic effects [15]. In addition, according to Swain [12], Pb, Ni, Cr and Zn also show adverse effects on the environment. Bearing in mind the toxic effect of the elements on the environment and the level of their emissions to the environment from the energy sector, the identification of their distribution between the products of combustion is necessary for the development of effective methods for reducing the emissions of those elements. The first step down this road is presented in this article and it concerns the distribution of the elements between the Coal Combustion Products (CCPs).

2. Experiments

2.1. Analytical Methods

Analytical samples were taken in accordance with the PN-G-04502:2014-11 standard. The ash content in the coal samples ash was determined in accordance with the PN-G-04512:1980/Az1:2002 standard. The concentration of the basic elements (Si, Al, Ca, Fe, Mg, Na, K) and the content of nickel, lead, chromium and zinc were determined with a Hitachi Z-2000 Atomic Absorption Spectrometer using the Zeeman background correction effect with the flame atomization (FAAS) mode. Table 1 lists the parameters of the FAAS method for the dispersion of each of the analysed elements along with the limit of detection of the analytical method (LOD). The uncertainty of ecotoxic elements content in the test samples was $\pm 1.5\text{ mg}_{\text{Ni}}/\text{kg} \pm 0.7\text{ mg}_{\text{Pb}}/\text{kg} \pm 5.1\text{ mg}_{\text{Cr}}/\text{kg} \pm 4.7\text{ mg}_{\text{Zn}}/\text{kg}$.

In order to perform the analyses on the FAAS, all samples were digested in the Berghoff SpeedWave4 microwave system. Nearly 130 mg of the sample were mineralized with the combination of nitric acid (V) and hydrofluoric acid. Subsequently, supersaturated boric acid was used as the complexing reagent.

Table 1. Selected measurement data for FAAS method.

	<i>Ni</i>	<i>Cr</i>	<i>Pb</i>	<i>Zn</i>
<i>Atomizer</i>	Standard burner			
<i>Gas</i>	C ₂ H ₂ + air			
<i>Slit width [nm]</i>	0.2	1.3	1.3	1.3
<i>Analytical spectral line [nm]</i>	232.0	359.3	283.3	213.9
<i>Atomization temperature [°C]</i>	≈ 2300			
<i>LOD [µg/ml]</i>	0.01	0.02	0.04	0.01

2.2. Sample analysis

Samples of the coal blends combusted in pulverised bed reactors and their CCPs were analysed, i.e.: daily mean fly ash samples, ash-slag mixtures and flue gas desulfurization products (gypsum and filter cakes). The samples came from two Polish power plants burning hard coal blends, originating from various mines of the Upper Silesian coal basin. Both power plants are equipped with the same flue gas treatment system consisting of the Selective Catalytic Reduction (SCR), the ESP and the installation of Wet Flue Gas Desulfurization (WFGD). In order to characterize the test samples, in Table 2 the contents of Si, Al, Ca, Fe, Mg, Na, K were collected.

Table 2. The concentration of Si, Al, Ca, Fe, Mg, Na, K in examined samples.

<i>Sample</i>	<i>Content of the elements [%]</i>													
	<i>Power Plant I</i>							<i>Power Plant II</i>						
	<i>Si</i>	<i>Al</i>	<i>Ca</i>	<i>K</i>	<i>Na</i>	<i>Mg</i>	<i>Fe</i>	<i>Si</i>	<i>Al</i>	<i>Ca</i>	<i>K</i>	<i>Na</i>	<i>Mg</i>	<i>Fe</i>
<i>Coal</i>	5.7	2.0	0.5	0.5	0.2	0.4	1.2	4.8	1.8	0.5	0.4	0.2	0.3	1.2
<i>Ash-slag</i>	18.3	10.1	2.7	2.2	0.4	1.7	6.3	20.9	8.8	2.0	1.8	0.5	1.2	6.9
<i>Fly ash</i>	20.3	11.2	2.5	2.5	0.5	1.6	4.3	17.2	9.3	2.5	2.0	1.3	1.5	6.1
<i>Gypsum</i>	0.28	0.06	-	0.02	0.00	0.04	0.04	0.30	0.05	-	0.02	0.01	0.01	0.04
<i>Filter cake</i>	6.2	2.3	15.9	0.8	0.1	0.8	1.5	5.7	2.0	16.4	0.8	0.1	0.9	2.4

3. Results and Discussion

The concentrations of the ecotoxic elements measured in the test samples are provided in Table 3. The analysed coal blends were characterised by high contents of the tested elements, much higher than the average world content of these elements in hard coals (except for the of nickel content in the coal blend originating from plant 2 for which those contents were similar). The ash content in the investigated coal blends was 22% and 11% in the case of the first and the second plants, respectively. This is important, as higher contents of the determined elements in coal have been reported for samples with higher ash contents.

Table 3. The concentration of the analysed ecotoxic elements in the samples.

Sample	Content of the ecotoxic elements [mg/kg]											
	Power Plant I				Power Plant II				Reference data			
	Cr	Ni	Pb	Zn	Cr	Ni	Pb	Zn	Cr	Ni	Pb	Zn
Coal	83.2	61.5	152.2	173.9	36.1	16.1	42.1	78.3	17.0	17.0	9.0	28.0 [4]
									12.3	9.0	23.4	33.0 [9]
Ash-slag	325.8	372.9	119.8	760.8	312.7	397.4	59.5	158.0	47.9	30.0	21.2	50.0 [9]
									153.0	74.0	30.0	174.0 [19]
Fly ash	99.6	107.9	372.2	830.6	65.1	86.6	332.2	486.5	76.2	64.4	155.2	270.3 [9]
									149.0	74.0	58.0	309.0 [19]
Gypsum	dl*	dl*	dl*	16.8	dl*	dl*	dl*	13.7	5.9	1.5	1.5	3.1 [9]
									5.0	4.0	1.4	<0.01 [19]
Filter cake	21.5	48.5	382.9	1 466.9	32.3	45.4	662.3	1 593.1	-	-	-	-

* dl – result is below the limit of detection

The content of Cr, Ni, and Pb in gypsum samples was below the detection limit of the applied method, which proves the lack or a very small content of ecotoxic elements in this material. The amount of zinc in gypsum for both power plants was relatively low and at the similar level. According to Cordoba et al. [16], the most likely form of zinc present in the samples is ZnFe_2O_4 . Therefore, it can be assumed that in the test samples of gypsum up to 8% of iron may be associated with zinc in the form of the above-mentioned compound.

In the flue gas desulfurization process, filter cakes (waste from residual water treatment) are another by-product apart from gypsum. The tested filter cake samples were characterized by a low content of chromium and nickel, which can be associated with a lower volatility of these elements and, thus, their lower concentration in fly ashes when compared to ash-slugs. On the other hand, this waste was enriched with lead and zinc, which, according to the literature [19], may be due to an increased content of these elements in the FGD-used sorbent materials. In the case of Zn, its high content in filter cakes can be a result of an increased content of this element in fly ash particles that can penetrate into the residual water and then be filtered.

The analysed elements were accumulated mainly in the ash-slugs fraction and fly ashes, which is consistent with the literature data [6-11, 17,19]. In the case of chromium and nickel noticeably higher values were registered for the ash-slugs samples. The ratio between the content of these elements in the fly ash and their content in ash-slugs (FA/AS, Table 4) was low. The reverse situation was noted for lead and zinc which mainly accumulated in the fly ashes (FA/AS for the lead was 3.1 and 5.6, depending on the plant, and in the case of zinc it was 1.1 and 3.1). This is due to the fact that at high temperatures these elements become volatile and condense on the particles of ash when the temperature drops. Since a number of ecotoxic elements in CCPs strictly depends on their contents in the combusted coal fuel, the Relative Enrichment Factor (REF) was determined as follows (1):

$$REF = \frac{\text{element concentration in fly ash (ash-slugs)}}{\text{element concentration in coal}} * \frac{\% \text{ash concentration in coal}}{100} \quad (1)$$

The REF values determined for the analysed elements are given in Table 4. Taking into account the behaviour of the ecotoxic elements during the combustion processes according to Meij and Winkel [18], these can be divided into three groups:

- group I – nonvolatile elements (REF for fly ash and bottom ash ~1),
- group II – volatile elements in the boiler, but complete condensation on the ash particles (REF for fly ash 1.3 - 4 (> 4) and for bottom ash < 0.7),
- group III – very volatile elements (REF for fly ash and bottom ash <1).

The results presented in Table 4 suggest that the tested elements do not belong to the group of nonvolatile elements. Instead, they can be classified as partially volatile elements, which enrich the ash-slag (Cr, Ni) or fly ash (Zn, Pb) in group I/II.

Table 4. The Relative Enrichment Factors for fly ash and ash-slag and FA/AS ratio*.

	<i>Ni</i>	<i>Cr</i>	<i>Pb</i>	<i>Zn</i>
<i>REF for Fly Ash</i>				
PP I	0.4	0.3	0.5	1.1
PP II	0.6	0.2	0.9	0.7
<i>REF for Ash-Slag</i>				
PP I	1.3	0.9	0.2	1.0
PP II	2.7	1.0	0.2	0.2
<i>FA/AS*</i>				
PP I	0.3	0.3	3.1	1.1
PP II	0.2	0.2	5.6	3.1

* the ratio of the element content in fly ash to its content in ash-slag

In order to determine the degree of accumulation of the elements in individual samples the Enrichment Factor was calculated (2):

$$EF = \frac{A_{TE}}{A_c} \quad (2)$$

EF – Enrichment Factor [-]

A_{TE} – the concentration of an element in a sample [mg/kg]

A_c – Clarke value of sedimentary rocks [mg/kg]

In addition, in order to compare the content of selected elements with their world average content in coal ashes the calculated coefficients were compared with the Coal Affinity Index (3) [4].

$$CAI = \frac{A_{PL}}{A_c} \quad (3)$$

CAI – Coal Affinity Index [-]

A_{PL} – the average concentration of an element in coal ashes [mg/kg]

In comparison with the CAI, the analysed ash-slugs samples were characterized by a higher enrichment factor for all the determined elements in the case of power plant I (Figure 1). For power plant (II) this indicator is considerably lower as a result of the lower content of the analysed elements in the coal blends and in the solid by-products of coal combustion.

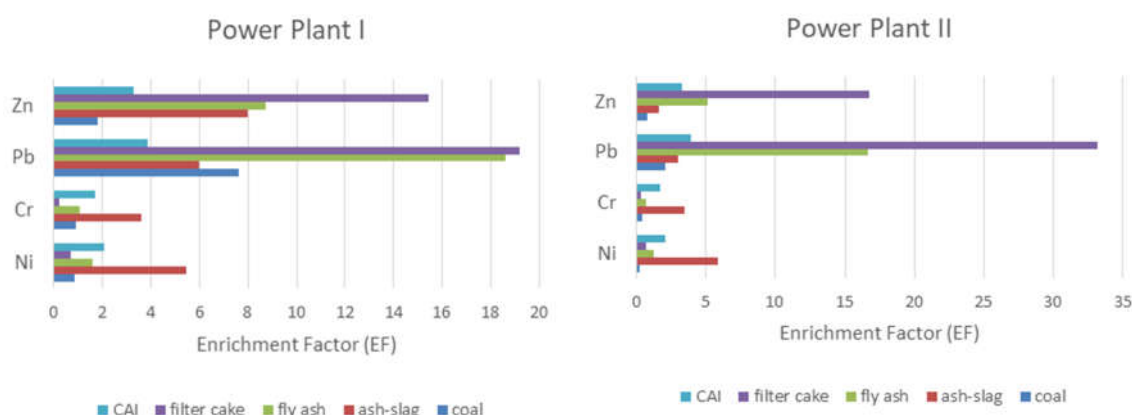


Figure 1. Enrichment factor specified for the tested samples.

It is noteworthy that the enrichment factors of lead and zinc for filter cakes were more than 8 and 5 times higher in comparison with the CAI for Pb and Zn, respectively. This proves the strong enrichment of this waste in these elements, much stronger than the one observed in the case of fly ash.

4. Conclusions

The purpose of the research was to determine the contents of Ni, Cr, Pb and Zn in coal blends and in the Coal Combustion Products (fly ash, ash-slag mixtures, gypsum and filter cakes). Based on the results of the analyses, the following conclusions can be drawn regarding the investigated coal blends and their combustion products:

- The coal blends had significantly higher contents of the determined elements than their world average contents in hard coal.
- The contents of the determined elements in the gypsum samples were below the limit of detection of the analytical method used, which is a proof of a small ecotoxic elements accumulation in this by-product.
- The examined elements were distributed primarily between the ash-slag samples and fly ash, of which the analysed ash-slags were more enriched with Ni and Cr (the ratio FA/AS was 0.2 – 0.3), while Zn and Pb are mostly accumulated in the fly-ashes (FA/AS: 1.1-5.6); such a distribution is also in agreement with the calculated Relative Enrichment Factors (these indicators take into account the different content of the above elements in carbon compounds).
- The filter cakes contained small amounts of chromium and nickel but were enriched with lead and zinc. The Enrichment Factor (EF) calculated for this waste was over 8 and 5 times higher for Pb and Zn, respectively, than the CAIs. This proves the high enrichment level of the filter cakes with ecotoxic elements.
- Based on the determined values of the REF's, in accordance with the classification proposed by Meij and Winkel [18], the analysed elements can be included in group I/II.

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