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CHANGE OF ZN, NI, AND CU CONTENT IN FLY ASH ON THE BASE OF THEIR MINERAL COMPOSITION

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Abstract. Fly ash is produced in the coal burning process in heat power plants equipped with electrofilters, located in the Upper Silesia Industrial Region (USIR). The collected material has been investigated by the following techniques: X-ray diffraction analysis powder method, analytical scanning electron microscopy (ASEM), spectrometric ICP method, as well as laser method (size analysis of fly ash). Fly ash has been investigated with respect to the size of its particles. Average content of such heavy metals as Ni, Cu, and Zn has been defined. Chemical composition of particles rich in heavy metals is of oxide and aluminosilicate nature. They have rarely been observed on the surface of the unburnt organic matter. The size of individual particles of fly ash, which are carriers of Cu, Zn, and Ni, ranges from 1 to 5 μm, and of aggregates — to 12 μm.

Key words: fly ash, heavy metals, chemical composition.

Abstrakt. Zbadano popioły lotne powstające podczas spalania węgli w elektrociepłowniach wyposażonych w elektrofiltry, zlokalizowanych na obszarze górnośląskiego obszaru przemysłowego. Zebrane próbki poddano badaniom rentgenostrukturalnym, mikroskopii skaningowej (ASEM), badaniom spektrometrycznym (ICP) oraz określono ich skład ziarnowy metodą laserową. Badania wykonano dla różnych frakcji ziarnowych popiołów. W próbkach określono zawartość Ni, Cu i Zn. Zaobserwowano, że skład chemiczny cząstek popiołu bogatych w metale ma charakter glinokrzemianów. Wielkość cząsteczek popiołu, które były nośnikami Ni, Cu i Zn, wahał się od 1 do 5 μm, a agregatów — do 12 μm.

Słowa kluczowe: popioły lotne, metale ciężkie, skład chemiczny.

INTRODUCTION

As a result of the coal burning process in heat power plants furnace, waste is generated in the form of fly ash and slag. Fly ash from pulverised-fuel fired furnaces accounts for around 70–85% of the total mass of furnace waste (Fulekar, Dave, 1986; Laudyn *et al*., 2000). Devices used to reduce dust pollution include primarily electrofilters with high and medium efficiency.

The emission of dust pollution from fuel burning in the Upper Silesia area amounted in 2002 to 25.6 thousand tons; and from plants posing a particular threat to the atmosphere — around 32.8 thousand tones (Statistical Yearbook, 2003). From the environmental protection point of view, the most important are very small-sized particles of ash (less than 1 μm). They are caught by electrofilters in small portions only and most of them enter atmosphere. Physical properties of fine-dispersion dust and its various chemical composition determine toxic properties of the air. The emission of dust in the Upper Silesia area accounts for 24% of the total dust emission in Poland. The particle size does not exceed 5 μm (Jabłońska *et al*., 2003). The finest particles of fly ash contain the highest amounts of heavy metals, such as lead, zinc, copper, and nickel (Querol *et al*., 1995; Minghou *et al*., 2003). They constitute a potential source of the atmosphere pollution and contamination of the remaining components of the atmosphere (Fytianos *et al*., 1998). Research shows that dust produced by industrial activities are more likely to induce allergic reactions in people than natural dust (Obtułowicz *et al*., 1996).

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METHODS

Samples of the fly ash have been taken during the process of coal burning in selected heat power plants located in the Upper Silesia Industrial Region (USIR). These heat power plants are equipped with dust collectors of electrofilter type, in which the effectiveness of dust collecting amounts to around 98%. The temperature in the combustion chamber was around 1000°C. The samples were taken directly from under the electrofilter as well as from before and behind the electrofilter.

Size analysis of fly ash was conducted with the use of laser apparatus 200LS-AC in order to define volume composition of the particles. Analyses performed by the analytical scanning method of electron microscopy were conducted with the use of the PHILIPS XL 30 TMP scanning electron microscope, as well as the JEOL JSM-540, with EDS microanalyser. Phase composition of the fly ash samples was analysed with the use of X-ray difractometer PHILIPS PW 3710. The content of trace elements were analysed by the ICP method with the use of spectrometers JARRELL ASH model Enviro and PERKIN ELMER in Activation Laboratories Ltd. in Canada.

RESULTS

In the research on the fly ash, the particles size distribution is very important. It is of particular significance especially when commenting on the harmfulness of ash to the environment. Average diameters of the particles were selected, dividing into particles smaller than 5 μm, 5–10 μm, 10–20 μm, and 20–60 μm, and larger than 60 μm. The results show a clear domination of particles with the diameter up to 20 μm. The results have been presented in Table 1.

Table 1

Average percentage distribution of fractions in fly ash from power plant

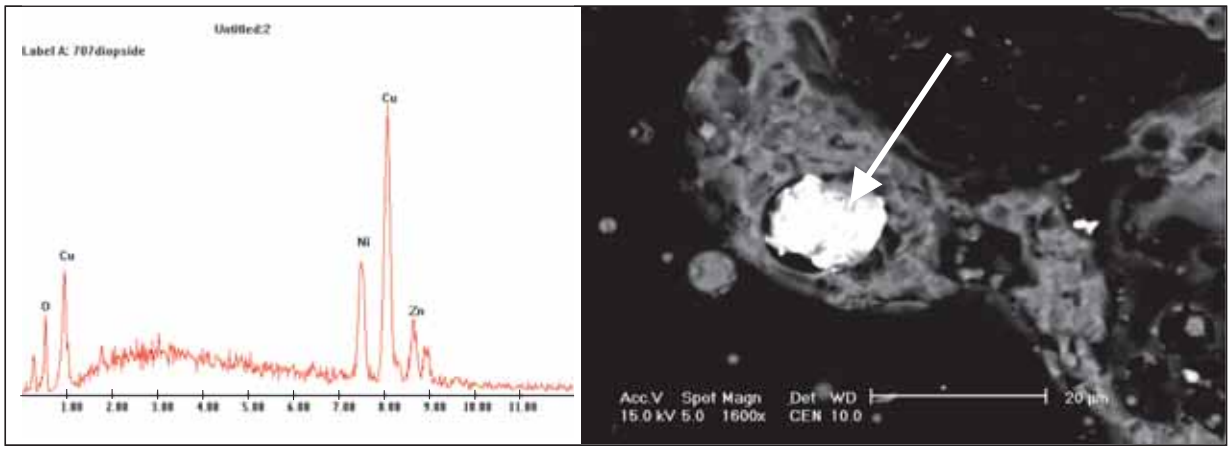
Fly ash	Diameters in the particles fly ash				
	<5 μm	5–10 μm	10–20 μm	20–60 μm	>60 μm
Under the electrofilter	21.00	20.80	42.00	9.80	6.40
Before the electrofilter	31.50	17.10	20.10	20.60	10.70
Behind the electrofilter	30.20	17.50	21.20	21.40	9.70

The applied research methods allowed to define the chemical composition of fly ash and average content of copper, nickel, and zinc. Copper, zinc, and nickel oxides were identified most commonly, as well as PbS substance and copper containing aluminosilicate phase. Unburnt organic matter was rarely a carrier of heavy metals. The marked components of fly ash were seen as single, irregular forms of up to 2 μm. Moreover, aggregates, mainly of Cu, Ni, and Zn oxides, ranging from 7 to 12 μm, were observed, occasionally with visible traces of dissolution. Particles under 0.5 μm were also observed, difficult to identify due to their very small sizes. Photographs of fly ash components containing heavy metals, made by the scanning method of electron microscopy have been presented on Figure 1. Average contents of the analysed heavy metals in the fly ash with respect to average diameters have been presented on Figure 2.

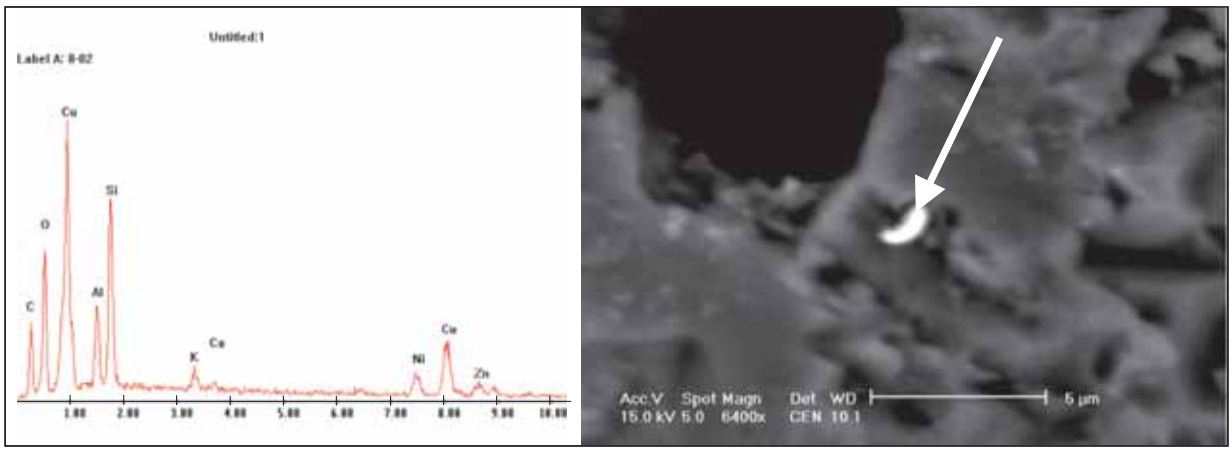
Results of the analyses indicate that the highest contents of nickel, copper, zinc, and lead were identified in the fly ash taken behind the electrofilter. The highest number of particles containing these elements was encountered in particles under 10 μm. The mineral composition is of aluminosilicate amorphous nature, contrary to the ash from under the electrofilter (mainly aggregates of Cu, Zn, and Ni oxides as well as unburnt organic matter). The share of the amorphous phase in the investigated fly ash was estimated at 55–70%.

It is most likely that the smallest particles (under 1 μm) containing the identified heavy metals easily come through electrofilters and enter the atmosphere where they undergo further physical and chemical transformations. Such components as substances PbS and ZnS as well as aluminosilicate phase containing heavy metals were observed in the atmospheric dust across the entire USIR area and also outside it (Jabłońska, 2003).

a) SEM image with EDS spectrum of an copper, zinc, and nickel oxides aggregate



b) SEM image with EDS spectrum of aluminosilicate particles containing copper



c) SEM image of zinc sulphide and “typical” EDS spectrum

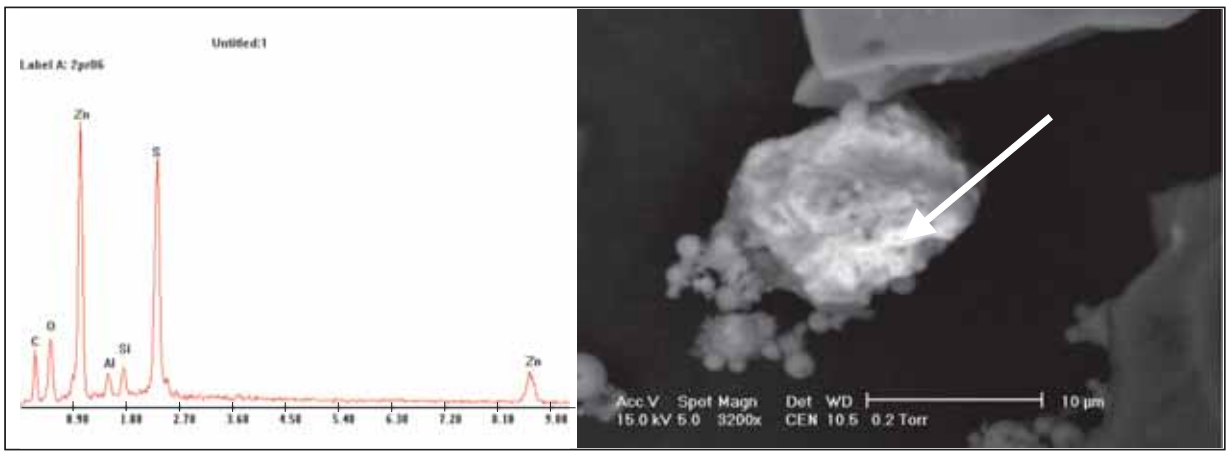


Fig. 1. Examples of the fly ash particles containing heavy metals

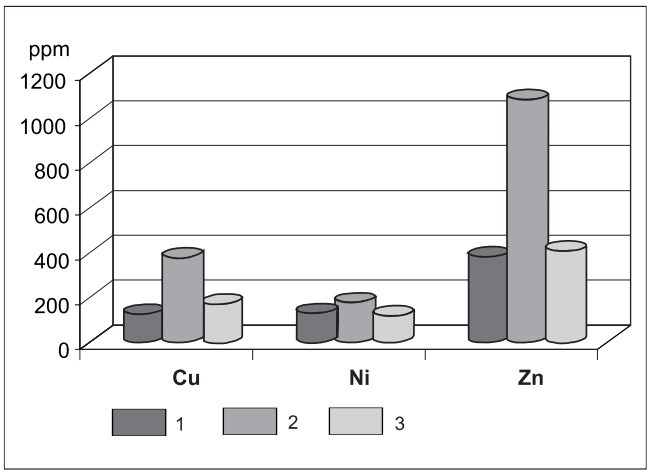


Fig. 2. Average contents of Cu, Ni, and Zn (ppm) in the fly ash

1 – before the electrofilter, *2* – behind the electrofilter, *3* – under the electrofilter

CONCLUSIONS

Carriers of particles containing heavy metals are aluminosilicate substance, oxides, and unburnt organic matter. The highest amounts of nickel, copper, and zinc were found in the fly ash taken behind the electrofilter. Copper, nickel, and zinc appear in aluminosilicate combinations, more rarely in oxide ones. Sizes of the analysed particles are smaller than 2 μm.

The smaller diameter of the fly ash particles, the higher was the number of components containing heavy metals. Small sizes of the fly ash particles in which nickel, copper, zinc, and lead were identified may have a negative impact on the cleanliness of the atmosphere and, simultaneously, on the health condition of the inhabitants. It is a long-term influence and its consequences are difficult to predict.

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