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Letter to Editor

Heavy Metals in Fly Ash from a Coal-Fired Power Station in Poland

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Abstract

The main subject of this study is fly ash created during coal combustion in Rybnik Power Station in Upper Silesia in the southern part of Poland. This is the biggest block power station in this region. Generated power is 1600 MW. Annual dust emission from professional energy in Upper Silesia is estimated at 32.8 thousand tons, which is about 22% of total national emissions. X-ray powder diffraction, Analytic Scanning Electron Microscopy (ASEM) and Induced Couple Mass Spectrometry (ICP- MS) methods have been applied extensively to heavy metals (Cu, Ni, Pb, Zn, Cr, Cd) content analysis and their host mineral phases identification. Concentrations of Cu, Ni, Pb, Zn, Cr and Cd as well as mineral composition of fly ash being their carriers have been specified. Average Zn concentrations in fly ash are 120 ppm, but for all other elements the averege concentrations were 38 ppm for Cu, 41 ppm for Ni, 44 ppm for Pb, 64 ppm for Cr and 3 ppm for Cd. Amorphic aluminosilicate substances, oxides and sulphides are mineral phases containing heavy metals. The sizes of these particles are up to 12 μm.

Keywords: power station, fly ash, heavy metals

Introduction

Upper Silesia is one of the most polluted areas of Poland. Dust emissions from professional energy of this region constitutes 22% of total dust emission in Poland [1]. Furnace wastes like fly ash and slugs are created in the process of coal combustion in power plants. Fly ash from dusty furnaces amounts to about 70-85% of grate mass of furnace wastes [2]. Electro filters with high and average efficiency are used for reduction of ash pollution in Polish power stations.

Emission of dust wastes in Upper Silesia in 2004 was 32.8 thousand tons, which is 22% of total dust emission in Poland [3]. Very small particles (<1 μm), which in small amounts are caught by electro filters while in majority penetrate the atmosphere, are most important for environmental preservation. The physical properties of fine dispersive dust and their various chemical compositions determines the toxic properties of air. The smallest particles of fly ash are enriched with heavy metals [4-8]. An indicator of heavy metal emissions from coal combustion processes is the specified condition of ash emission indicator. This is a result of comparison between the amount of coal used (56 million tons per year) [3] for energy production in Poland and poorly satisfying average efficiency of dust-collecting devices, mainly in towns boiler rooms and in heat-generating plants. Power stations have the smallest contribution to national heavy metal emissions in spite of using the largest amount of coal. Fly ash emitted from professional industry are mostly spherical and their diameters are up to 2 micrometers [9].

Fly ash is a potential source of pollution not only for the atmosphere but also for the other components of the environment. Their deposition in storage places can have negative influences on water and soil because of their

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granulometric and mineral composition as well grain morphology and filtration properties.

Studies have revealed that dusts from industry have greater ability to developing allergic diseases than natural ones [10]. Additionally, they have negative influence on plants – mainly forests [1-11]. They show a harmful influence on flora, mainly forests, choking stomatal apparatuses of plants, impeding photosynthesis by sunlight screening and, as a result, decreasing CO_2 assimilation. Atmospheric pollution related to dust emission caused by coal combustion and secondary dusting from waste dumps results in human and animal illnesses. Epidemiologists indicate a relationship between high concentrations of atmospheric pollution and morbidity of such illnesses as chronic bronchitis and lung cancer.

Methods

Samples of fly ash come from coal combustion in Rybnik Power Station (Poland), whose power is 1600 MW (8 blocks, 200MW each). Annual coal consumption is over 3.6 million tons. The power station is equipped for fume desulphatization and electrofilters. Flying ash was sampled in the process of semi-arid combustion gas desulphurization (desulphurization efficiency was 70-85%). The process applying cold ash reaction occurs in the reactor at 80–130°C. It comes from the electrofilter area where there is the highest calcium oxide concentration. The reaction is activated by introducing material containing base compounds with the addition of calcium and sodium hydroxides together with water from the skimming system.The studied samples have been collected directly from under electro filter funnels during 2003-04. We analyzed 25 samples of fly ash together.

Analysis have been performed using analytical scanning electron microscopy method with scanning electron microscopes PHILIPS XL 30 TMP, JEOL JSM-5410 equipped with EDS and unified with Noran Instruments software and HITACHI S-4700 with NORAN Vantage microanalytic system (Laboratory of Scanning Microscopy, Jagiellonian University in Cracow) under analytical conditions such as acceleration voltage 20-25 kV and beam current intensity 20 nA. Analyses were performed on carbon rings and polished pellets (the samples were mounted in epoxy resin).

The fly ash phase composition was examined by a PHILIPS PW 3710 X-ray diffractometer. The following measurement conditions have been applied: lamp voltage – 45 kV, current intensity – 30 mA, time of impulses

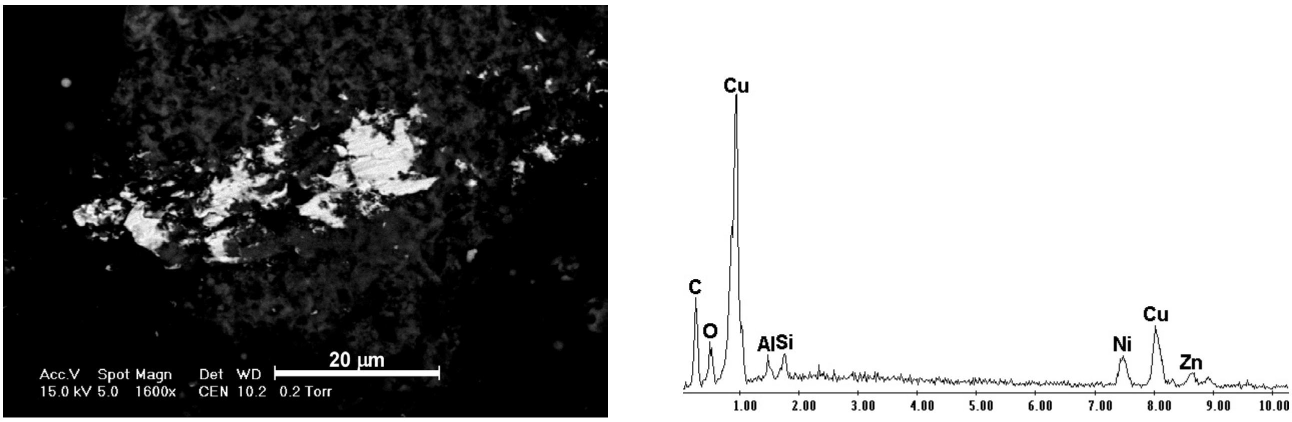

Fig. 1. SEM image with EDS spectrum of Ni, Cu and Zn oxides in fly ash from Rybnik Power Station.

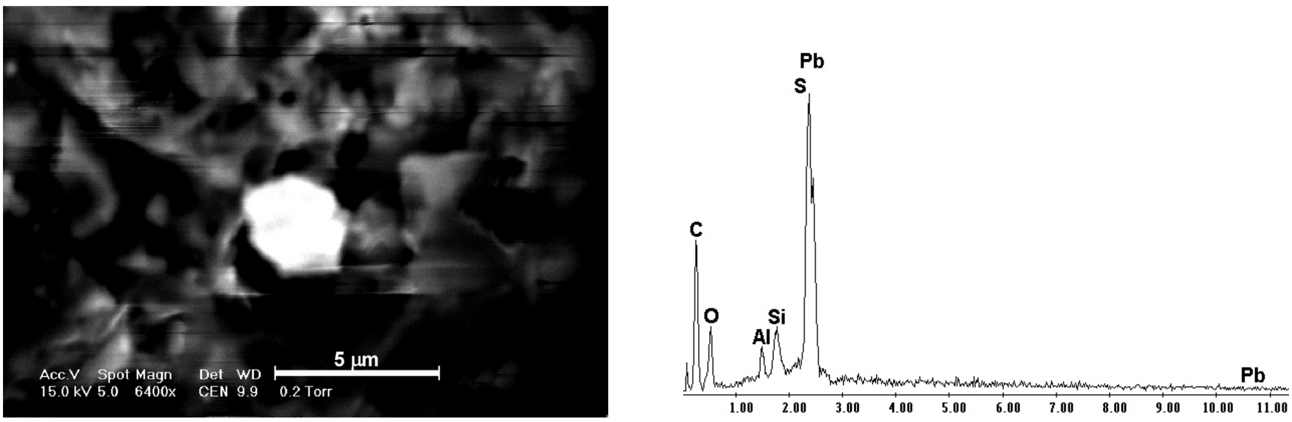

Fig. 2. SEM image with EDS spectrum of PbS in fly ash from Rybnik Power Station.

counting in the step method was 2 and 3 second (per a step), counter speed was 0.01^0 and 0.02^0 per minute. The estimated concentrations (%) of the analyzed mineral components are given using the X'PERT computer program.

Contents of trace elements have been established by ICP and ICP-MS methods using JARRELL ASH Enviro model and PERKIN ELMER spectrometers in Activation Laboratories Ltd., Canada. Determinations were performed dissolving flying ash. To this aim a 0.25g sample was dissolved in 10 ml HCl-HNO_3- $HClO_4$-HF at 200°C, and next the extracts were filled up to 10 ml with diluted aqua regiatrace. The instrument operated by inductively coupled plasma mass spectrometry (ICP-MS): R_f power 900 W, argon plasma flow 16 l/min, argon nebulizer flow 0.8 l/min, argon auxiliary flow 0.7 l/min.

Results and Discussion

The share of particular trace elements is pretty much on the same level of concentration (Cu – 55ppm, Ni –78 ppm, Pb – 67 ppm). However, the maximal concentrations have been obtained for zinc (120 ppm) and those concentrations are in agreement with published results of fly ash studies conducted by different authors in different scientific centres [12-14].

The average concentration of Cu, Ni, Pb and Zn determined in coal burned in the Rybnik Power Station is lower than that from fly ash and is equal to 24g/t (Cu), 24 g/t (Ni), 18 g/t (Pb), 45 g/t (Zn), 38 g/t (Cr) and 5 g/t (Cd).

The applied methods of studying allowed determination of the mineral composition of the fly ash particles which are the heavy metal carriers. Cu, Zn, Pb and Ni oxides have been identified (Fig. 1). Lead sulphates and chlorides (Fig. 2) as well as aluminosilicate phase containing varied amounts of Cu, Ni, Pb and Zn have been determined. The aluminosilicate particles have an amorphic character confirmed by X-ray studies.

Fly ash difractograms had high background and a "hump" characteristic for amorphic substance in the range of 20-35°2Θ. The share of amorphic phase in fly ash is estimated at 55-70 wt%. The estimated concentration of amorphic substance has been given by the X'PERT computer program.

Fly ash containing heavy metals occur as single irregular sharp-edged particles with size smaller than 2μm. Moreover, they form characteristic aggregates of Cu, Ni and Zn oxides with sizes in the range of 7 μm to 12 μm. Particles smaller than 0.5 μm have been noticed but they are difficult to identify due to their small diameters.

The smallest particles of fly ash (< 1 μm) containing the identified heavy metals readily pass through the electro filters to the atmosphere, where they undergo further physical and chemical transformations. The results of fly ash studies in selected localities of Upper Silesia clearly point to the dominant role of anthropogenic components [1]. The most important sources of tropospheric pollution are not the factories of professional industry but ash from so-called low emissions, that come from coal combustion in home fireplaces and boiler rooms of housing estates that do not possess any facilities for reduction of dusty and gaseous pollution.

Summary

Results of studies confirm the pro-ecological activities conducted by Rybnik Power Station in the vicinity of burned coal quality improvement and the technology of this process.

The average concentration of Ni, Cu and Pb in analyzed samples of fly ash does not exceed 45 ppm. Oxides, aluminosilicatic substance, sulphides and chlorides (Pb mainly) play the role of heavy metal carriers. The sizes of single particles and aggregates do not exceed 2 and 12 μm, respectively. Cu, Ni and Zn occur within aluminosilicatic and oxide linkage, but Pb most often occur as sulphides and chlorides. However, the amorphic phases in fly ash, which amount to 70 wt%, are far easier solved than the crystal substance with the same composition. It is necessary to pay particular attention to this process mainly in the case of fly ash deposition in disposal places.

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