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GEOCHEMICAL ANALYSIS OF KOSTOLAC POWER PLANT FLY ASH: WORKING AND LIVING ENVIRONMENT INFLUENCE ASPECT

Abstract: *The aim of this study is geochemical analysis of flying ash generated by the combustion of lignite in the Kostolac A and B thermal power plants. The fractionation procedure of fly ash samples was done firstly, and then stereomicroscopy, FTIR, SEM / EDS and ICP-OES analyzes. The contents of heavy metals V, Cr, Mn, Co, Ni, Cu, Zn, Cd and Pb were determined. The results showed that the concentrations of the tested heavy metals are within the limits that are not harmful to the human health. However, the mineralogical analysis of the mentioned ash indicates that the present glass and other high-temperature mineralogical components can cause respiratory problems and disfunction of other organs of the inhabitants of Kostolac and the immediate surrounding. The tested fly ash, also, can be used as a material in various fields of industry (e.g. construction).*

Key words: lignite, fly ash, Kostolac, heavy metals.

INTRODUCTION

Kostolac basin represents one of the economically most important deposits of lignite, which is an important energy resource in Serbia. [1] The exploitation of lignite on a large surface allows the operation of two thermal power plants „Kostolac A" and "Kostolac B" with a total installed power of 921 MW.

These two power plants (Figure 1) burn more than 25,000 tons of coal every day, and produce more than 5,500 tons of ash as a product of combustion. Kostolac thermal power plants generate about 3 700 GWh of electricity, which represents c.a. 11% of the total electricity production in the electric power system of Serbia. [2]

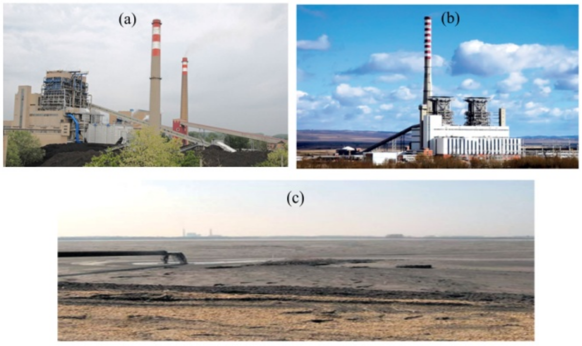

Figure 1. *Kostolac thermal power plants: Kostolac A (a), Kostolac B (b), place to dispose of the ashes (c)*

In the last decade, lignite has been exploited from three surface mines Ćirikovac, Klenovnik and Drmno. Since 2009, Drmno mine is only active for lignite exploitation. Lignite combustion in power plants produces large quantities of gas and solid waste products that endanger the environment. Modern research has shown that knowledge of geochemical, mineralogical and petrological characteristics of coal and its combustion products is very important for better utilization and more reliable protection of the environment. [2]

Geographical location

Kostolac coal basin (Figure 2) covers the area between the river Morava in the west, Golubac mountains in the east, the Danube river in the north and the Mlava basin in the south. The total area of the basin is 400 km^2.

Kostolac coal basin encompasses an area of 100 km^2 in the municipality of Pozarevac. The city Kostolac is located 80 km south-east of Belgrade.

Figure 2. *Geographical location of Kostolac coal basin*

Lignite reserves are estimated at about 400 million tons. This deposit originated in the upper Miocene, probably in the shallow lake of the Pannonian basin. [1]

Today, in the Kostolac district, about 2,500 hectares of land, which is about 5% of the city of Požarevac, is used for the needs of the thermal power plant (deposition of piles, plants).

Flying ash is deposited and mixed with demineralized water in a ratio of 1:10 in three cassettes, and then samples from each cassette were taken for this investigation.

Fly ash

Electro filter ash (also called "fly ash") is formed as a waste product in the process of coal combustion in thermal power plants. During combustion process most of the inorganic matter segregates as ash. The fly ash is hydraulically deposited on landfills that are usually located in the vicinity of the thermal power plant. A small part (about 1%) of the total aspect of the coal combustion process flows through the chimney into the atmosphere, while the rest is deposited as solid waste in the landfill. The amount of ash deposited by a thermal power plant, depending on its capacity, is measured in millions of tons per year. This presents a huge economic and environmental problem in all countries around the world, far ahead of other industrial waste, such as phospho-, fluoro- gypsum and various industrial sludges, etc. [3]

The characteristics of fly ash depend on the type of coal and the type of method used when the ash is collected from electrostatic precipitators. It is mostly fine-grained and powdery material. The colour of the ash is usually gray and depends on the content of Fe_2O_3 and the amount of unburned coal in the ash. The ash particles are of different sizes, mainly of spherical shape, although particles of irregular shape can be found as well. The particle size of the ash is from about 0.01 to about 100 μm in diameter, with largest grain size of about 20 μm. [4]

The chemical composition of ash, as well as its physical properties, depends on the type of coal used in the thermal power plant. Ash contains SiO_2, Al_2O_3, Fe_2O_3 and CaO as the most important chemical compounds, and to a lesser extent MgO, MnO, Na_2O, K_2O, SO_3, N and C. The composition of the fly ash mainly included inorganic components (crystalline and amorphous), organic substances and liquids, gaseous and gas-liquid inclusions in inorganic and organic components.

During the combustion process, inorganic components form crystalline and amorphous phases, of which the ash is composed. Calcite largely exceeds the CaO, which in some cases can react with SO_2 and CO_2 and form anhydride (gypsum) and calcite again. Clay and feldspar, melt and transform into a glass. Kaolinite usually transforms to the glass and sometimes cristobalite, while other types of clay and feldspar convert into the glass. Quartz is partially melted, or the quartz grains are slightly remained in the melting process.

The spherical particles of which the glass (amorphous) ash consists mainly of thin, hollow, ceramic microspheres called the cenospheres (Figure 3).

The composition of their solid crust includes aluminosilicate glass, mullite, quartz, calcite, Fe-oxides, Ca-silicates and sulfates. These spheres are formed under specific conditions, such as molten drops of clay minerals, mica, feldspar and quartz. Spheres are usually filled with gases arising from the combustion of organic matter, decomposition of carbonates, clay mineral dehydration and evaporation of water from the pores. These are generally CO_2, N_2, O_2 and H_2O. It is assumed that these spheres are formed at temperatures between 1230 and 1400 °C. Cenospheres in whose cavities are much less spherical particles called plerosfere (Figure 3). In the ash of lignite, bituminous and anthracite coal there are also ferrospheres (Figure 3), which consist of ferispinel, which are solid solutions of magnetite with the content of Mg, Mn and Ca, hematite, and to a lesser extent, ilmenite and chromite. Ceramic cenospheres, as well as magnetic ferrosphere can be concentrated by special methods and as such can have industrial application. For example, the ferrospheres are used as catalysts in the processes of high temperature metal conversion. In addition to the amorphous phase and crystalline phases, soot particles can also be found in ash, and sometimes minerals such as barite, anglezite, apatite and monacite. [5]

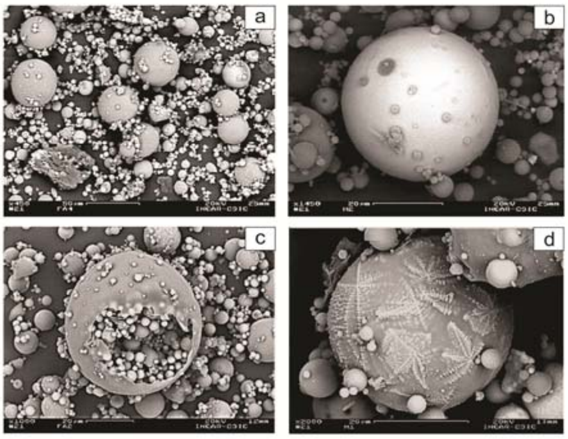

Figure 3. *The amorphous phase, consisting of spherical aluminosilicate particles in fly ash (a); alumosilicate spherical particles (b); alumosilicate plerosfera in ashes (c); and ferosfera with dendritic magnetite crystallization (d) [5]*

PAPER ATTRIBUTES

Three samples of fly ash from Kostolac basin were investigated. Samples were taken from the ash dumps located in the vicinity of the power plant Kostolac.

Fractionation procedure

In order to determine the concentrations of investigated metals and mineralogical composition of the fly ash samples, the method of sequential dissolution using the corresponding mineral acids was used (Figure 4).

Pre-treatment

Firstly, the samples were dried in an oven at a temperature of from 200 °C in order to determine the percentage of moisture, which is approximately 15 %.

Before treatment with mineral acids, the samples were grinded in a vibrating mill to a particle size of 100 µm. [6, 7]. The flow chart in Fig. 4 outlines the major steps in preparing the four fractions of fly ash samples from Kostolac basin.

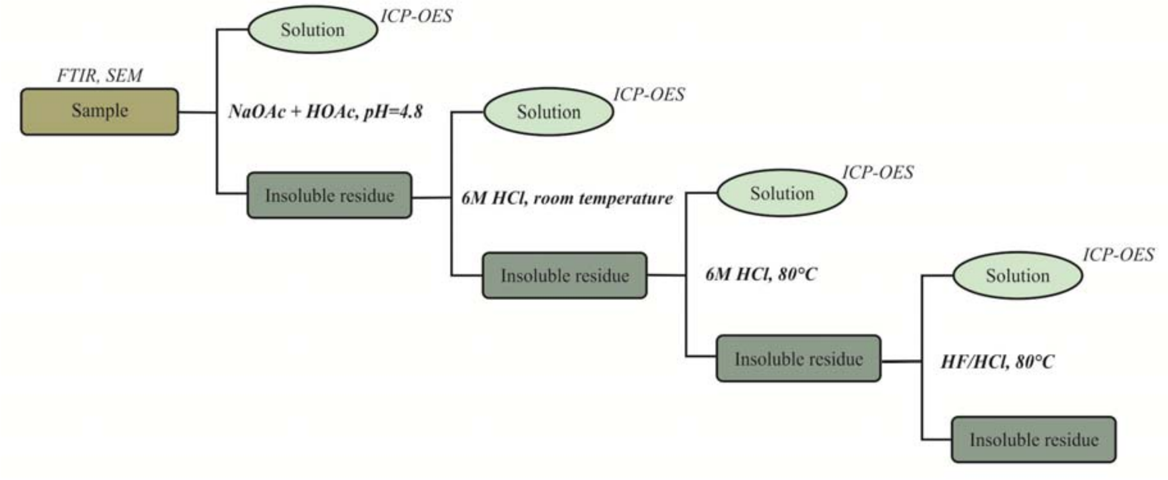

Figure 4. *Fractionation procedure*

<u>Dissolution in acetate buffer</u>

The powdered sample (1,00 g) was added in small amounts to 25 mL of 1 M acetate buffer (CH_3COOH/CH_3COONa, pH = 4.8). After that, the solution was mixed on a magnetic stirrer, without heat, for 12 hours, then centrifuged and rinsed with distilled water to a negative reaction to acetate. The residue was dried in an electric oven at 105 °C and measured. The difference between the masses of untreated sample and insoluble residue equals the percentage of fractions soluble in acetate buffer. The soluble material constitutes the carbonate fraction. The concentration of the metals investigated was determined from the solution using ICP-OES.

<u>Dissolution in cold HCl</u>

The insoluble residue was further demineralized by the treatment with cold 6 M HCl. The solution was stirred on a magnetic stirrer for 12 hours. After stirring, the solution was centrifuged and washed until the quantitative removing of chloride occurred. The soluble material constitutes the fraction of metal oxides and hardly soluble carbonates. The concentration of studied metals in solution was determined by ICP-OES.

<u>Dissolution in boiling HCl</u>

An exactly measured mass of the sample after treating with cold HCl was added in small quantities in warm (80 °C) 6 M HCl. After that, the solution was stirred with a magnetic stirrer for 12 hours, and the solution was centrifuged and washed until the quantitative removing of chloride occurred. The concentration of metals investigated was determined as mentioned before.

<u>Dissolution in a mixture of HF/HCl</u>

Dissolving the sample with a mixture of HF/HCl is used to remove silicate. Accurately weighed mass of insoluble residues after previous treating was added in small portions to the mixture of 22 M HF and 12 M HCl [3:1 (v/v)], in a Teflon beaker. The solution was heated with continuous stirring at 80 °C and, if necessary, a mixture of acids can be added to the complete dissolution of silicate minerals. The solution is evaporated to a small volume, after which 20 ml of 12 M HCl was added, to remove the excess HF, and then re-evaporated to a volume of about 10 ml. After stirring, the solution was centrifuged and washed until the quantitative elimination of chloride. The concentration of metals investigated was determined as mentioned before. The insoluble residue represents the organic fraction.

Fourier Transform Infrared (FTIR) spectroscopy

The functional groups available in the untreated samples were detected by the KBr technique using FTIR spectroscopy (Bomem, Hartman & Braun MB-100 spectrometer). The spectra were recorded at room temperature in the range from 4000 to 400 cm^{-1}. The KBr pastilles were prepared from 1.50 mg of finely powdered samples dispersed in 150.00 mg of anhydrous KBr. The obtained FTIR spectra were analyzed using Win Bomem Easy software. FTIR analyses of the whole samples were performed in the Spectroscopy Laboratory (Faculty of Technology, Leskovac).

Inductive coupled plasma-optical emission spectroscopy (ICP-OES)

ICP-OES analysis of fractions were carried out in the Laboratory of Physical Chemistry, Institute of Nuclear Sciences Vinča in Belgrade, on ICP-OES spectrometer, Spectroflame (power of 2.5 kW and a frequency of 27.12 MHz), the company Spectro (Germany).

Scanning Electron Microscopy (SEM)

SEM/EDS images and elementary analysis were performed at the University Center for Electron Microscopy, Faculty of Medicine in Nis, on JEOL JSM-5300 electron microscope with Tracor TN-2000 energy-dispersive X-ray spectrometer.

Before analyzing, samples were molded on a brass substrate and deposited in a vacuum with argon, a thin layer of gold. To record, an acceleration voltage of 30 keV with a current jet of 0.1 microns was used.

RESULTS AND DISCUSSION

The results of fly ash solubility were obtained based on fractional analysis which is shown in Table 1. As it is shown, the greatest part of the samples consists of silicate, which is later confirmed by FTIR analysis. Also, there are some clay minerals, oxides and carbonates.

Table 1. *Results of fly ash fractionation*

Fraction	[mass %]
Acetate bufer	9
Cold HCl	8
Hot HCl	10
HF/HCl	73

Stereomicroscopic characterization of investigated samples is shown on Figure 5 before (a) and after the treatment by cold HCl (b) and boiling HCl (c). Based on these observations, it was determined that the fly ash consists of very fine particles having a diameter < 10 mm, have a large surface area and very fine texture. In addition, the ash is composed of a solid material which has been subjected to high temperatures > 1,000 °C. In the atmosphere, most of these materials are unstable and is transformed into the thermodynamically more stable forms of minerals.

Figure 5. *The stereomicroscope pictures of fly ash samples (a) before and after treatment with cold (b), and boiling (c) HCl.*

FTIR analysis showed that in untreated samples, there were some carbonate minerals (peak at 1652 cm^{-1}). It, also, contains oxides and clay minerals (bands below 800 cm^{-1}), but the biggest part of the waste was silicate minerals (1090 cm^{-1}). Based on the FTIR spectra shown on Figure 6, it can be seen that this type of ash contains mostly aluminosilicate glass and quartz. SEM/EDS analysis showed results that were in correlation with those that can be found in the literature. [5]

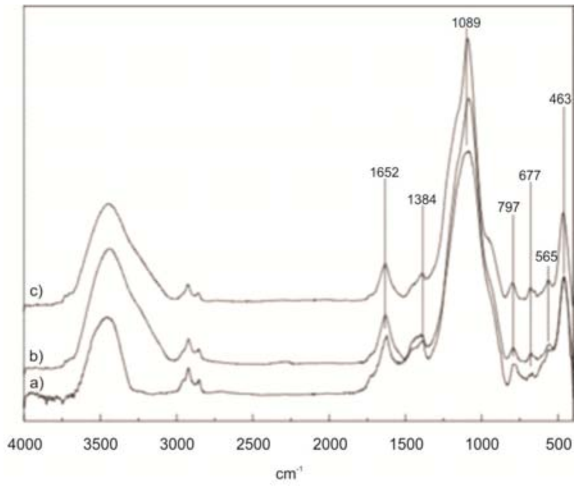

Figure 6. *FTIR spectra of untreated samples of Kostolac fly ash*

Figure 7 shows the results of the measurements of the concentration of heavy metals in the fly ash in fractions obtained by ICP-OES.

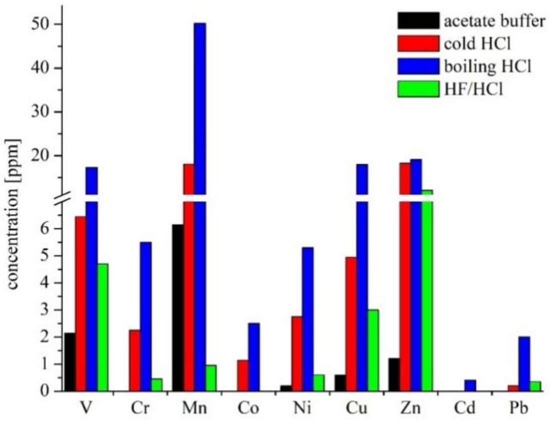

Figure 7. *Heavy metals content in fly ash [ppm]*

Heavy metals represent a serious environmental problem because of frequent use in industry and as a result of the human activity. They can be detected in all phases of environment (air, water, land). Also, they can chronically affect human health through contaminated air, food and water. Through accumulation in the internal organs, they manifest a hepatotoxic, nephrotoxic and neuroacoustic effect. [8]

Obtained content of vanadium in the analyzed samples was from 2.15 to 17.30 ppm in the studied fractions. The largest part of V is concentrated in smectite minerals.

Chromium was not detected in the carbonate fraction, due to a low affinity of this metal to form carbonates, while in the rest of the fractions its contents are from 0.45 ppm in silicate fraction up to 5.5 ppm in smectite fraction.

As shown in Figure 7, the concentrations of manganese in the tested samples were 5.18 ppm in the fraction which is soluble in cold HCl, and 50.20 ppm in the fraction that is soluble in hot HCl. The smallest part of the Mn is concentrated in the fraction which is soluble in a mixture of HF/HCl (0.95 ppm).

Content of cobalt in the analyzed samples are in range from 1.15 to 2.50 ppm. It is interesting that the carbonate and silicate fraction did not contain Co, while most of the nickel is concentrated in the silicate fraction (5.30 ppm)

The content of copper in the tested samples ranges from 0.60 to 18.00 ppm. The largest part of Cu is concentrated in the clay fraction. The lowest concentration of Cu is in the carbonate fraction (as expected Cu rarely builds carbonates).

Zinc content range in the analyzed samples is 1.20 ppm in acetic fraction. Most of it is in minerals that make up the oxide and clay fraction (18.25 and 19.10 ppm).

Toxic cadmium was detected only in the clay fraction (0.40 ppm). Thus, it is interesting to note the absence of this metal in the other (carbonate, oxide and silicate), but also very important regard to its toxicity. Lead is present mostly in the clay fraction (2.00 ppm). It is found in similar quantities in the oxide (0.20 ppm) and silicate (0.35 ppm) fraction, while the carbonate is not detected, or it can be noted as absence of lead in this fraction.

As can be seen from the ICP-OES analysis in comparison with maximally allowed concentrations of investigated metals, fly ash from Kostolac thermal power plant does not contain enlarged concentrations of metals. The concentrations of the tested heavy metals are within the limits that are not harmful to the human health. However, the mineralogical analysis of the mentioned ash indicates that the present glass and other high-temperature mineralogical components can be the cause of the respiratory problems and may negatively affect other organs of the inhabitants of Kostolac and the nearest surrounding. Also, as these tested metals have a cumulative effect, exposure for a long period to the ash could lead to serious health consequences [8].

The tested fly ash, also, can be used as a material in various fields of industry (e.g. construction) [9, 10, 11].

CONCLUSION

Fractional analysis showed that the carbonate-oxide fraction ranges from 25-48%, 34-38% of a smectite, and silicate fraction was 8%. ICP-OES analyses show that the contents of heavy metals in investigated fly ash were within the limits that are not harmful to the human health, while the mineralogical analysis indicated potential harmful influence on respiratory systems and other organs of the inhabitants of Kostolac and the nearest surrounding.

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BIOGRAPHY

Dragan M. Đorđević was born in Pirot, Serbia, in 1973.
He received the diploma in general chemistry (1998) and the Ph.D. degree in chemistry (2009) from the University of Niš, Faculty of Sciences and Mathematics, Department of Chemistry.
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GEOHEMIJSKA ANALIZA LETEĆEG PEPELA IZ TERMO ELEKTRANE KOSTOLAC SA ASPEKTA UTICAJA NA ŽIVOTNU I RADNU SREDINU

Dragan Đorđević, Maja Stanković, Nenad Krstić, Vladimir Dimitrijević, Nemanja Anastasijević, Miloš Đorđević, Milica Nikolić

Rezime: *Cilj ove studije je da se uradi geohemijska analiza letećeg pepela koji nastaje sagorevanjem lignita u termoelektranama Kostolac A i B. Uzorci pepela su prvo podvrgnuti procesu frakcinacije, a zatim su urađene stereo-mikroskopija, FTIR, SEM/EDS i ICP-OES analize. Ispitivan je sadržaj metala V, Cr, Mn, Co, Ni, Cu, Zn, Cd i Pb. Rezultati su pokazali da su koncentracije ispitivanih teških metala u granicama koje nisu štetne po zdravlje stanovništva. Međutim, mineraloška analiza navedenog pepela ukazuje da prisutna stakla i ostale visokotemperaturne mineraloške komponente mogu biti uzročnici oboljenja disajnih i drugih organa stanovnika Kostolca i neposredne okoline. Ispitivani leteći pepeo može se koristiti i kao materijal u različitim oblastima industrije (građevinarstvo i dr.).*

Ključne reči: lignit, leteći pepeo, Kostolac, teški metali.