EVALUATION OF POTENTIAL POLLUTION OF NATURAL WATER BY TRACE ELEMENTS ORIGINATING FROM POWER PLANT ASHES

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Abstract

Coal ashes (flay ash and bottom ash) from pawer plants contain trace elements that have been possible pollutants of surface and ground waters. Some of trace elements in coal ashes are naturally radioactive and make possible risk of radiation.
Because of that the examination of leaching of trace elements from coal ashes and determination of radioactivity of coal ashes are very important information for safe disposal of them, without harmful impact to environment (water, soil).
In this work the extracts of fly ash and bottom ash from the Serbian "Nicola Tesla" power plant was analyzed by atomic absorption spectroscopy to determine the concentration of Cu, Zn, Cd, Pb, Ni, Mn, Cr, Sb, Fe and Al in them. Also, it was determined the radioactive contamination of the mentioned ashes (the specific activity of the radioactive nuclides: ^{238}U, ^{235}U, ^{40}K, ^{226}Ra, ^{232}Th).
The results obtained by atomic absorption spectroscopy have shown that the concentrations of Cd and Pb in the extracts of flay ash and bottom ashes from the "Nicola Tesla" power plant are higher than it is limited in Italian and German lows for safe disposal of coal ashes (there is no Serbian low about it). Consequently, potential pollution of natural water by Cd and Pb from disposal sites of the "Nicola Tesla" power plant could be possible, according to the mentioned low.
The results of the determination of the radioactive contamination of the ashes from the "Nicola Tesla" power plant showed that they did not exceed the permissible limits, according to Serbian regulation. On this way, these results indicate that eventually dissolution of radioactive nuclides from disposal sites of the "Nicola Tesla" power plant in natural water could not be harmful, very probably.

***Key words**: Pollution of natural water, Fly ash, bottom ash*

Introduction

Approximately 80% of the solid residue from pulverized fuel combustion is released as fly ash (FA); the rest, consisting of larger particles, is mostly retained within the furnace as bottom ash (BA). The properties of FA and BA depend on the physical and chemical properties of the coal source, the coal particle size, the burning process, and the type of ash collector (Jankowski, J. et al., 2005).
The chemical composition of FA and BA is very complex. They have organic and inorganic constituents. The organic constituents contains unburnt coal components. The inorganic part consists of non-crystalline amorphous components and crystalline components: silicates, oxides and hydroxides, sulphates, carbonates, phosphates, sulphides and others (accessory minerals and phases). (Vassilev, S., Vassilev, C., 1996).
A number of so called "trace elements" (Cu, Zn, Cd, Hg, As, Pb, Sb, Cr etc.) could be present in the coal ashes in lower but significant concentrations. They are commonly present as impurities in the glass (amorphous) phases and are included in the crystalline components of ashes. Trace elements are mainly enriched in fine-grained fractions of ashes (Vassilev, S., Vassilev, C.,1997).
Coal, like most materials found in a nature, contains trace quantities of naturally occurring radionuclides: ^{238}U, ^{232}Th and ^{40}K. During coal combustion most of the uranium, thorium and their decay products are released from the original coal matrix and are distributed between the gas phase and solid combustion products (ashes). Less volatile elements such as uranium, thorium and majority of their decay products are almost entirely retained in the solid combustion wastes (Evangelau, P.,.1996)
During combustion, the volume of coal is reduced by over 85 %, which increases the concentrations of the metals originally in the coal.

Since trace elements are potentially hazardous substances, improper disposal and utilization of fly ash and bottom ash could cause undesirable environmental effects, For example they may be extracted in natural waters (surface and groundwater).

Because of that the leaching behavior of fly ash and bottom ash and the determination of the radioactivity of these ashes are of great importance for an evaluation of adverse environmental impact of their disposal or utilization.

The “Nikola Tesla” power plant is the biggest power plant in Serbia. It is producing about 5 – 6 million tones of coal ashes (fly ash and bottom ash) per annum.

These ashes are disposed by the wet disposal method in a slurry form to nearby waste-disposal sites. The disposal sites are located in the area rich in ground and surface waters. Consequently, the potential contamination of the surrounding waters and the water of river Sava (which is the final recipient of waters from the power plant disposal sites) is an ecological problem.

The present study investigated the content of ten metals (Cu, Zn, Cd, Pb, Ni, Mn, Cr, Sb, Fe and Al) in the extracts of fly ash and bottom ash from the Serbian “Nikola Tesla” power plant. Also, it was determined the radioactive contamination of the mentioned ashes (the specific activity of the radioactive nuclides: ^{238}U, ^{235}U, ^{40}K, ^{226}Ra, ^{232}Th).

Experimental

The chemical composition (presented as oxide equivalents) of fly ash and bottom ash from the Serbian “Nikola Tesla” power plant was determined by classic chemical analysis.

Concentration of trace elements in fly ash and bottom ash was determinated by atomic absorption spectrophotometric method using Perkin Elmer “’Analyst 300” spectrophotometer.

The mineralogical composition of FA and BA was determined by the XRD powder technique usinga Philips PW 1729 X-ray generator and a Philips PW 1710 diffractometer.

The radioactive contamination of the ashes from the “Nicola Tesla” power plant (the specific activity of the radioactive nuclides present in the fly ash and bottom ash) was study by gamma spectrometric analysis. The obtained results were compared with the maximum permissible specific activity of radioactive nuclides, according to the standard used in our country (SRPS Official Register No 8/87). Also, on the bases of these results, the so-called radioactive coefficients, were calculated according to the Polish BN-87/6713-02 standards. Namely, according to these standards (Wyszomirski, P., Beylska, E., 1996) , the radioactivity are determined by the following coefficients:

$$f_1 = 0.00027\ S_K + 0.0027\ S_{Ra} + 0.0043\ S_{Th} \text{ and } f_2 = S_{Ra},$$

where S_K, S_{Ra} and S_{Th} are the specific activity (in Bq/kg) of ^{40}K, ^{226}Ra and ^{232}Th, respectively.

Leaching behavior of fly ash and bottom ash was examined according to method which has been developed by the European Committee for Standardization (CEN procedure B) using tap water as medium (Pelleg, S. , Cohen, H.,1999). This method consisted of placing 100 g of dry ash in 1000 cm^3 of tap water (pH=5,5), agitation during 24 h (5 rpm) and than filtration of suspension ash-water. Liquid phase (extracts of fly ash and bottom ash) than was analyzed by atomic absorption spectroscopy (Perkin Elmer “’Analyst 300” spectrophotometer).

Results and discussion

Chemical composition of fly ash and bottom ash

On the basis of the chemical analysis it was evident that the fly ash from the Nicola Tesla power plant can be classified as a low calcium fly ash (class F, according to ASTM 618). This fly ash satisfies the chemical requirements for use as a pozzolon, because the content of pozzolan oxides (SiO_2+Al_2O_3+Fe_2O_3) in it (80.66 %) is greater than the minimum content for these oxides required by ASTM 618 (70 %). Also, the contents of SO_3 (2.74 %) and Na_2O (0.41 %), as well as the L.O.I. (1.85 %) are lower than allowed maximum values proposed by ASTM 618 (5 %, 1.5 % and 6 %, respectively).

The content of oxides: SiO_2 ,Al_2O_3 and Fe_2O_3 were lower (49.39%, 19.70% and 5.83%) but loss on ignition higher (8.91 %) in the bottom ash from the Nicola Tesla power plant than in the fly ash.

The concentrations of trace elements in the fly ash and bottom ash, determined by atomic absorption spectroscopy, are presented in Table 1.

Table 1 The concentrations of trace elements in the fly ash and bottom ash, mg/kg

Elements	Fly ash	Bottom ash
Cu	263	200
Zn	190	124
Cd	0.52	0.25
Pb	102	72
Ni	175	155
Mn	317	222
Cr	275	205
Sb	3.3	4.1
Fe	90.9	99

The results presented in table 1. showed that in general the concentration of trace elements in fly ash was higher than in bottom ash.

Mineralogical composition of of fly ash and bottom ash

On the basis of X-ray diffraction study it can be stated that the major crystalline phase in the fly ash is quartz-SiO_2. The other crystalline phase in fly ash, present in small amounts, were: mulite-$Al_6Si_2O_{13}$, anhydite-$CaSO_4$, feldspar-$NaAlSi_3O_8$, diopside-$CaMgSi_2O_6$, hematite-Fe_2O_3 and gehlenite-$Ca_2Si_2O_7$. In the bottom ash, the major crystalline phase was quartz, then calcite-$CaCO_3$ and small amounts of anhydrite, feldspar, diopsid and hematite.
Besides the mentioned crystalline phases, a significant amount of amorphous aluminosilicates (glass) are represented by the broad " hump" in the XRD pattern of fly ash and bottom ash. The SiO_2 present as quartz or in the crystalline aluminosilucates phase is inert. Similarly, the part of the alumina in the crystalline phase is inactive. Both the silica and alumina in the amorphous aluminosilcates (glass) are reactive.

Leaching behavior of fly ash and bottom ash

The results of leaching test, e.g., the concentration of trace elements present in extracts of fly ash and bottom ash from the "Nicola Tesla" power plant are presented in Table 2. Also, the regulatory limits for leachates for landfill non-hazardous and hazardous waste in the Germany (Van der Sloot, H., 1996) and the standards limits established by Italian legislation for leachates for solid waste disposal (Mangialard, T. et al, 1999) are given in Table 2.

The regulatory limits for trace elements in extracts of wastes for landfill in Germany (Table 2) are done on the basis of DIN 38414 S4 leaching procedure which consists of placing solid wastes in distilled water (liquid/solid ratio = 10) and continuous agitation for 24 h. This procedure was almost the same as the procedure applied in our work (we used tap water instead to distilled water).

The Italian legislation for leachates for solid waste disposal is based of the Italian standard acetic acid leaching test which consists of contacting a given amount of solid material with distilled water (liquid/solid ratio = 16), for 24 h, and keeping the pH at 5 by addition of 0.5 M acetic acid solution.

Table 2. Concentration of trace elements in FA and BA extracts and regulatory limits

Element	BA extract	FA extract	Limit value [a]	Limit value [b]	Limit valu [c]
Cu	<0.1ppm	<0.1ppm	5 ppm	10 ppm	0.1 ppm
Zn	0.5 ppm	0.6 ppm	5 ppm	10 ppm	-
Cd	0.1 ppm	0.2 ppm	0.1 ppm	0.5 ppm	0.02 ppm
Pb	2 ppm	3 ppm	1 ppm	2 ppm	0.2 ppm
Ni	1 ppm	1 ppm	1 ppm	2 ppm	-
Mn	0.2 ppm	0.3 ppm	-	-	-
Cr	<0.1ppm	<0.1ppm	-	-	Cr(VI) 0.1ppm
Sb	4 ppm	7 ppm	-	-	-
Fe	3 ppm	2.6 ppm	-	-	-
Al	3 ppm	2 ppm	-	-	-

[a] Regulatory limits for leachates for landfill non-hazardous waste in Germany
[b] Regulatory limits for leachates for landfill hazardous waste in Germany
[c] Standard limits for leachates for solid waste disposal in Italy

Comparing the our results (the contents of Cu, Zn, Cd, Pb and Ni) with the regulatory limits applied in Germany it is evident that bottom ash from the “Nicola Tesla” power plant require landfill as hazardous material (only concentrations of Cu and Zn in its extract were bellow limit value for leachates for landfill non-hazardous waste). The fly ash from the “Nicola Tesla “ power plant is much hazardous than bottom ash, because its extract contained Pb (3 ppm) even above the limit value (2 ppm) for landfill hazardous waste.
Because the regulation in Italy are stronger that in Germany, bottom ash and fly ash from the “Nicola Tesla “ power plant do not satisfy the conditions for any safe disposal according to Italian regulation (the contents of Cd in the extracts of BA and FA were 5 and 10 times greater than limit value, respectively; the contents of Pb in the extracts of BA and FA were 10 and 15 times greater than limit value, respectively).

The radioactivity of the coal ashes

The results obtained for the specific activity of the radioactive nuclides present in the ashes from the “Nicola Tesla” power plant and the calculated radioactive coefficients of these ashes are presented in Table 3.

Table 3. Gamma spectrometric analysis of the ashes

Radioactive nuclides and radioactive coefficients	Fly ash	Bottom ash	Permissible values
^{238}U (Bq/kg)	129 $\pm$ 36	161 $\pm$ 42	-
^{235}U (Bq/kg)	10 $\pm$ 1	6.3 $\pm$ 0.8	-
^{40}K (Bq/kg)	396 $\pm$ 40	358 $\pm$ 36	5000 *
^{226}Ra (Bq/kg)	126 $\pm$ 13	86 $\pm$ 8	400 *
^{232}Th (Bq/kg)	86 $\pm$ 9	63 $\pm$ 6	300*
Coefficient f_1	0.7323 – 0.910 Bq/kg	0.5426 – 0.656 Bq/kg	$\leq$ 1 Bq/kg**
Coefficient f_2	126 $\pm$ 13	86 $\pm$ 8	$\leq$ 185 Bq/kg**

* According to SRPS Official Register No 8/87
** According to Polish BN-87/6713-02 standards

The results in Table 3. show that the radioactive contamination of the ashes from the “Nicola Tesla” power plant do not exceed the permissible limits.

Conclusion

On the basis of our examinations it could be concluded:
1. When the composition of the Serbian Nicola Tesla" power plant fly ash extract and bottom ash extract are compared with German criteria (Van der Sloot, A.,1996), it is observed that fly ash extract is hazardous due to the cadmium and lead contents, and the bottom ash extract is hazardous due to lead content (in Serbia there are no any criteria about it).
Consequently, these wastes should be disposed by widely applied solidification/stabilization process, using cement or another inorganic binder.
Solidification/stabilization (S/S) process refers to changes in the physical and chemical properties of ashes due to the hydration reactions in the mixture coal ashes-cement.
The fly ash from the "Nicola Tesla" power plant has high content of pozzolan oxides (SiO_2+Al_2O_3+Fe_2O_3 = 80.66 %) and significant amount of amorphous aluminosilicates (glass) which means that it can easy react with cement forming calcium silicate hyrates (C-S-H) and calcium-aluminate-sulphate hydrate-ettringite (Et). It is believed, that formation of these compounds (C-S-H and Et) is mainly responsible for high strength of the treated coal ashes and heavy metal immobilization in them.
For this purpose, coal ashes-binder mixtures and their characteristics (water demand, setting time, mechanical strength and leaching properties) should be object of the feature examinations.
2. Because the radioactive contamination of the ashes from the "Nicola Tesla" power plant do not exceed the permissible limits (according to SRPS Official Register No 8/87 and according to Polish BN-87/6713-02 standards) it is real to expect that dissolved concentrations of the radioactive elements from them in natural water will be below levels of human health concern.

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