ANALYSIS OF NATURAL RADIONUCLIDES IN COAL, SLAG AND ASH IN COAL-FIRED POWER PLANTS IN SERBIA

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Abstract

The radioactivity monitoring in the "Nikola Tesla", "Kolubara", "Morava" and "Kostolac" coal-fired power plants was performed by the Radiation and Environmental Protection Laboratory, Vinča Institute of nuclear sciences in the period 2003-2010. Monitoring included the analysis of soil, water, flying ash, slag, coal and plants. This paper presents the results of the radioactivity analysis of coal, ash and slag samples. Naturally occurring radionuclides ^{226}Ra, ^{232}Th, ^{40}K, ^{235}U, ^{238}U, and ^{210}Pb as well as the man-made radionuclide ^{137}Cs were determined by gamma spectrometry using HPGe detector. The concentrations of pairs of radionuclides were statistically tested to determine the corellation between them. Based on the obtained results, health effect due to the activity of these radionuclides was estimated via radium equivalent (Ra_{eq}), external hazard index (H_{ex}), external gamma absorbed dose rate ($\dot{D}$) and annual effective dose.

Keywords: Radioactivity; Coal; Ash; Slag.

1. Introduction

The concept of technologically enhanced natural radioactivity (TE NORM) was introduced in the mid-seventies. It represents the unintentional exposure to natural sources of radiation which would not exist without the technological activity [1]. Earlier studies have shown that the main sources of technologically enhanced natural radioactivity are coal-fired power plants and artificial fertilizers applied in agriculture. Coal-fired power plants have been neglected as a radiation source for a long time. They

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became important for investigations as a result of the advancement of the scientific knowledge of biological effects of radiation on humans and after dose limits reduction in international recommendations and standards.

Coal combustion in power plants leads to a redistribution of natural radionuclides originating from coal, and to their concentration in ash and slag. The basic problem of technologically enhanced natural radioactivity caused by coal-fired power plants is the increase of the background gamma radiation level. Therefore, the local population is exposed to higher gamma radiation doses than in absence of coal-fired power plant.

In the combustion process, most of the mineral material in coal is converted into ash. Coal, like most materials found in nature, contains trace quantities of naturally occurring radionuclides, ^{238}U, ^{232}Th and ^{40}K [2]. Combustion of coal thus enhances natural radiation in the vicinity of the coal-fired power plants by release of these radionuclides and their daughters into the surrounding ecosystem. Unlike most of the nuclear and hydroelectric power plants, coal-fired power plants in Serbia are generally located in areas which are thickly populated and hence, the environmental impact and health impact experienced by the neighboring population is significant.

In the period 2003-2010 as a part of regular control of working and living environment of coal-fired power plants: "Nikola Tesla", "Kolubara", "Morava" and "Kostolac", the coal, ash and slag samples taken in the vicinity of the power plants have been analyzed. Based on the part of these analysis, health effect due to the activity of present radionuclides was estimated via radium equivalent (Ra_{eq}), external hazard indedx (H_{ex}), absorbed dose rate ($\dot{D}$) and annual effective dose.

2. Experimental

The coal, ash and slag samples were collected from various sites in the vicinity and inside the power plants. Samples were taken in "Nikola Tesla" coal-fired power plant during 2003, 2004, 2007, 2008 2009 and 2010, "Kolubara" during 2004, 2009 and 2010, "Morava" during 2004, 2007, 2008, 2009 and 2010 and "Kostolac" during 2005, 2006, 2007, 2008 and 2009. The coal and slag samples were provided by the responsible services in the power plants, while the ash was sampled in ash ponds in the vicinity of power plants. The sampling sites were chosen in such a manner, that the representative collection of samples could be obtained. Also, sampling sites were denoted by their GPS coordinates in order to enable us to repeat sampling in the same sites in following years. Coal, slag and ash samples were dried at 105^0C, sifted, weighed and sealed in Marinelli beakers. In order to achieve radioactive equilibrium, the sealed samples were left in the laboratory for 30 days prior to the measurement.

The samples were counted using two CANBERRA high purity germanium detectors (HPGe) with relative efficiency of 23 % and 20% and energy resolution of 1.8 keV at the 1332 keV ^{60}Co peak. The calibration was performed using the soil matrix spiked with ^{22}Na, ^{57}Co, ^{60}Co, ^{89}Y, ^{133}Ba, ^{137}Cs, total activity of 1.5 kBq kg^{-1}, at

reference date 01.07.1991., issued by National Office of Measures, Budapest, MIX-OMH-SZ. The results were then fitted by the exponential curve. All samples were measured for 70000s. The activity of ^{226}Ra and ^{232}Th was determined via their decay products: ^{214}Bi (609, 1120 and 1764 keV), ^{214}Pb (352 and 295 keV) and ^{228}Ac (338 and 911 keV), respectively. ^{235}U was determined via 185.7 keV corrected for ^{226}Ra. ^{238}U was determined via ^{234}Th (63 keV) or by ^{234}Pa ($t_{1/2}$ = 1.17 min, 1000 keV). The activity of ^{137}Cs was determined from its 661 keV energy. The activities of ^{40}K were determined from its 1460 keV γ-energy.

3. Results and discussion

In the samples of coal, slag and ash, the natural radionuclides (^{226}Ra, ^{232}Th, ^{40}K, ^{235}U, ^{238}U, ^{210}Pb) were detected. The mean values and range of obtained concentrations of naturally occurring radionuclides in the analyzed samples are presented in Table 1. The combined uncertainty of the results, originating from counting uncertainty, measuring of sample mass and uncertainty arising from fitting of the efficiency

calibration curve, was estimated to range from 10% to 40%.

The concentrations of natural radionuclides in coal and slag are lower compared to the concentrations found in ash, i.e., maximum concentrations were obtained in flying ash samples. The difference between concentrations of naturally occurring radionuclides in ash from passive and active ash pond are negligible and do not exceed the statistical variance. According to UNSCEAR [1], the mean natural radionuclide concentration expected in coal is 35 Bq kg^{-1} (range: 17–60) for ^{226}Ra, 30 Bq kg^{-1} (range: 11–64) for ^{232}Th and 400 Bq kg^{-1} (range: 140–850) for ^{40}K. As one sees from Table 1, the radionuclide concentrations in coal samples from the Serbian power plants are in the range of coal reported in UNSCEAR [1]. The activity ratio ^{235}U/^{238}U, corresponds to natural uranium in all samples. The range and average of natural radioactivity concentrations in coal, fly ash and slag samples reported in the present study are similar to those obtained for the Poland, India, China and Turkey power plant samples [3-6], except for the slag samples where the activity concentrations obtained in

Table 1. Range and mean value of measured concentrations of radionuclides in coal, slag and ash samples from investigated coal-fired power plants

	^{226}Ra [Bq kg^{-1}]		^{232}Th [Bq kg^{-1}]		^{40}K [Bq kg^{-1}]		^{238}U [Bq kg^{-1}]		^{235}U [Bq kg^{-1}]	
	range	mean	range	mean	range	mean	range	mean	range	mean
coal	14-52	29	Nov-32	21	45-243	120	18-71	43	0.9-3.6	2.1
slag	17-114	65	14-73	39	67-375	241	26-145	81	1.0-9.5	4.4
flying ash	45-270	120	29-121	72	174-489	360	21-246	129	1.4-14	7.3
ash active pond	71-139	101	54-90	73	250-429	361	59-236	134	3.8-10.4	7.1
ash passive pond	41-135	103	30-101	72	241-482	349	48-177	114	2.8-11	6.4

this study are slightly lower than the concentrations in the slag samples reported for the Poland power plant [3].

For all gathered samples in all power plants, basic statistical analysis was performed. Analysis included calculation of correlation factor given by [7].

$$r_{xy} = \frac{\sum_i x_i y_i - (1/n)\sum_i x_i \sum_i y_i}{\sqrt{\left[\sum_i x_i^2 - (1/n)\left(\sum_i x_i\right)^2\right]\left[\sum_i y_i^2 - (1/n)\left(\sum_i y_i\right)^2\right]}} \quad ...(1)$$

The analysis showed an apparent correlation between the specific activities of detected radionuclides. Strong correlation is noticed between ^{226}Ra and ^{238}U (correlation coefficient r = 0.86), ^{226}Ra and ^{232}Th (correlation coefficient r = 0.87), ^{232}Th and ^{40}K (correlation coefficient r = 0.87) and ^{226}Ra and ^{40}K (correlation coefficient r = 0.86), while a slightly lower correlation appears between ^{238}U and ^{40}K (correlation coefficient r = 0.79).

The distribution of ^{226}Ra, ^{232}Th and ^{40}K in environment is not uniform. Uniformity with respect to exposure to radiation has been defined in terms of radium equivalent activity (Ra$_{eq}$) in Bq kg^{-1} in order to compare the specific activity of materials containing different amounts of ^{226}Ra, ^{232}Th and ^{40}K. It is calculated using the following relation [8, 9]:

$$Ra_{eq} = C_{Ra} + 1.43C_{Th} + 0.077C_K \quad ...(2)$$

where C_{Ra}, C_{Th} and C_K are the activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K in Bqkg^{-1}, respectively. While defining Ra$_{eq}$ activity according to Eq. (2), it has been assumed that 370 Bq kg^{-1} of ^{226}Ra or 259 Bq kg^{-1} of ^{232}Th or 4810 Bq kg^{-1} of ^{40}K produce the same gamma dose rate.

The external gamma absorbed dose rate in the air at 1m above ground level was calculated from the measured activities of ^{226}Ra, ^{232}Th and ^{40}K in ash, assuming that the other radionuclides, such as ^{137}Cs, ^{90}Sr and the ^{235}U series can be neglected as they contribute insignificantly to the total dose from environmental background [10, 11, 12]. The calculations were performed according to the following equation 1:

$$\dot{D} = 0.462C_{Ra} + 0.604C_{Th} + 0.042C_K \quad ..(3)$$

where represents the dose rate in nGy h^{-1} and C_{Ra}, C_{Th} and C_K are the specific activities *(*Bq kg^{-1}*)* of ^{226}Ra, ^{232}Th and ^{40}K, respectively. In the above equation, it is assumed that all decay products of ^{226}Ra and ^{232}Th are in radioactive equilibrium with their precursors.

The external hazard index, H$_{ex}$, is defined as [7].

$$H_{ex} = C_{Ra}/370 + C_{Th}/259 + C_K/4810 \quad ..(4)$$

where C_{Ra}, C_{Th} and C_K are the specific activities (Bq kg^{-1}) of ^{226}Ra, ^{232}Th and ^{40}K, respectively. The value of this index must be less than unity in order to keep the radiation hazard insignificant. The maximum value of H$_{ex}$ equal to unity corresponds to the upper limit of radium equivalent activity (370 Bq kg^{-1}).

To estimate the annual effective dose, the following must be taken into account: (a) the conversion coefficient from absorbed dose in air to effective dose and (b) the indoor occupancy factor. Using the dose rate data obtained from the concentration values of natural radionuclides in soil, adopting the conversion factor of 0.7 SvGy^{-1} 1 from absorbed dose rate in air to effective dose received by adults and considering that people, on the average, spend 20% of their

time outdoors 1, the annual effective doses are calculated:

Annual effective dose

$[Sv] = [Gyh^{-1}] \times 24 \times 365 \times 0.7 \times 0.2 \qquad ...(5)$

Obtained results for Ra_{eq}, H_{ex}, and annual effective dose are presented in Table 2 in terms of mean values over the investigated time range for every power plant. These indeces were calculated for ash only (pond ash and flying ash), since coal and slag are localized within the power plants, and are not distributed in the environment. Ra_{eq} ranged

Table 2. Range and mean value of calculated radium equivalent (Ra_{eq}), external hazard index (H_{ex}), external gamma absorbed dose rate () and annual effective dose in ash samples from investigated coal-fired power plants

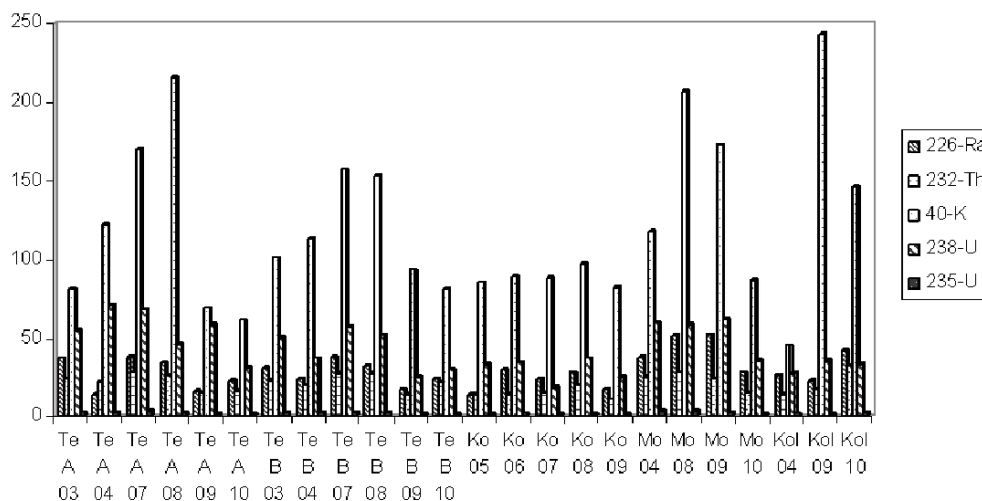|	Ra_{eq} [Bq kg^{-1}]		H_{ex} [Bq kg^{-1}]		[nGy h^{-1}]		annual effective dose [mSv]	
	range	mean	range	mean	range	mean	range	mean
Nikola Tesla A	182-308	253	0.49-0.83	0.68	83-139	115	0.10-0.17	1.4
Nikola Tesla B	102-325	236	0.28-0.88	0.64	47-147	107	0.058-0.18	1.3
Kostolac	105-152	120	0.28-0.40	0.33	48-70	55	0.059-0.085	0.67
Morava	164-405	253	0.44-1.1	0.68	76-186	116	0.093-0.23	1.4
Kolubara	170-316	232	0.64-0.85	0.63	78-142	106	0.096-0.17	1.3

Figure 1. Measured concentration of radionuclides in coal in coal-fired power plant Te A - "Nikola Tesla A", Te B - "Nikola Tesla B", Ko - "Kostolac", Mo - "Morava" and Kol - "Kolubara". Numbers 03, 04, 07, 08, 09 and 10 denote the years 2003, 2004, 2007, 2008, 2009 and 2010.
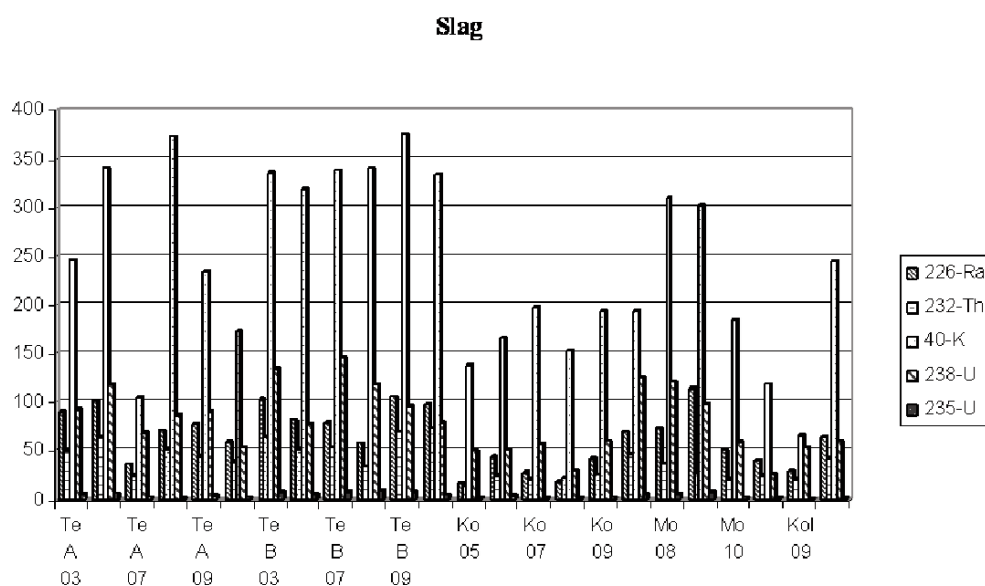
Slag

Figure 2. Measured concentration of radionuclides in slag in coal-fired power plant Te A - "Nikola Tesla A", Te B - "Nikola Tesla B", Ko - "Kostolac", Mo - "Morava" and Kol - "Kolubara". Numbers 03, 04, 07, 08, 09 and 10 denote the years 2003, 2004, 2007, 2008, 2009 and 2010.
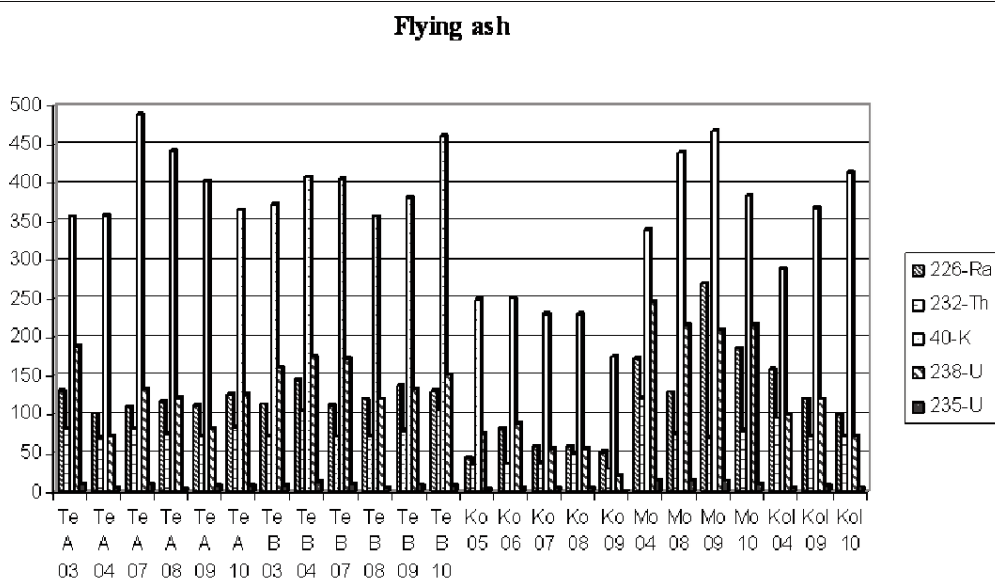
Flying ash

Figure 3. Measured concentration of radionuclides in flying ash in coal-fired power plant Te A - "Nikola Tesla A", Te B - "Nikola Tesla B", Ko - "Kostolac", Mo - "Morava" and Kol - "Kolubara". Numbers 03, 04, 07, 08, 09 and 10 denote the years 2003, 2004, 2007, 2008, 2009 and 2010.

from 101-401 Bq kg^{-1}, H_{ex} ranged from 0.28-0.88 Bq kg^{-1}, D from 47-186 nGy h^{-1} and the range of annual effective dose was from 0.09-1.4 mSv. As it can bee seen, Ra_{eq}

and H_{ex} are below upper limits (370 Bq kg^{-1} and 1 respectively) recommended by [1]. The other two indeces are similar to those reported in the literature for other countries, such as Poland, India, Gemany, Turkey and Australia [3-6].

Figures 1-3 show the results obtained for the activity concentrations for coal, slag and ash samples collected in all investigated power plants.

4. Conclusions

The obtained concentrations of naturally occurring radionuclides in all analyzed samples (coal, ash and slag) taken in the vicinity of the power plants in Serbia: "Nikola Tesla", "Kolubara", "Morava" and "Kostolac", are of the same order of magnitude compared to the other investigated coal-fired power plants in the world. According to the regulations and recommendations of IAEA and Serbian law, the by-products of coal-fired power plants investigated in this paper can be utilized as a component for building material, thus providing practical use and effective disposal of waste. The technology for this is now in development. Also, it can be concluded that the ash pond does not significantly endanger human health and environment, meaning that the production of energy in Serbian coal – fired power plants does not contribute significantly to TE NORM.

Acknowledgements

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