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EVALUATION OF RADIONUCLIDE CONTAMINATION OF SOIL, COAL ASH AND ZEOLITIC MATERIALS FROM FIGUEIRA THERMOELECTRIC POWER PLANT

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ABSTRACT

Neutron activation analysis and gamma-ray spectrometry was used to determine 238U, 226Ra, 228Ra, 210Pb, 232Th and 40K contents in feed pulverized coal, bottom ash, fly ash from cyclone and baghouse filters, zeolites synthesized from the ashes and two different soil samples. All the samples used in the study was collected at Figueira thermoelectric power plant, located in the city of Figueira, Paraná State, which coal presents a significant amount of uranium concentration. The natural radionuclide concentrations in pulverized coal were 4216 Bq kg^{-1} for ^{238}U, 180 Bq kg^{-1} for ^{226}Ra, 27 Bq kg^{-1} for ^{228}Ra, 28 Bq kg^{-1} for ^{232}Th and 192 Bq kg^{-1} for ^{40}K. The ashes fraction presented concentrations ranging from 683.5 to 1479 Bq kg^{-1} for ^{238}U, from 484 to 1086 Bq kg^{-1} for ^{226}Ra, from 291 to 1891 Bq kg^{-1} for ^{210}Pb, from 67 to 111 Bq $kg^{-1}$for ^{228}Ra, from 80 to 87 Bq kg^{-1} for ^{232}Th and from 489 to 718 Bq kg^{-1} for ^{40}K. Similar ranges were observed for zeolites. The activity concentration of ^{238}U was higher than worldwide average concentration for all samples. The concentration of the uranium series found in the ashes were lower than the values observed in similar studies carried out 10 years ago and under the limit adopted by the Brazilian guideline (CNEN-NN-4.01). Nevertheless, the concentrations of this specific area are higher than others coal mines and thermoelectric power plants in and out of Brazil, so it is advisable to evaluate the environmental impact of the installation.

1. INTRODUCTION

Coal, like most materials found in nature, contains trace quantities of the naturally occurring primordial radionuclides arising from the U and Th series and ^{40}K. Naturally occurring radionuclides contribute most to environmental radiation.
The concentration of these long lived radionuclides is usually low in the coal. However, some types of coal contain considerably higher amounts of natural radionuclides [1].
The coal used in Brazilian coal-fired power plants is pulverized and burned inside the boiler, producing bottom ash (15–20%), which falls inside the boiler, and fly-ash (80–85%) that is suspended in the flue-gas together with vapors of volatile elements. The natural radionuclides are distributed among these fractions.
The combustion of the coal leads to an increase of the natural radionuclides and non-combustible elements with enrichments factor in the ashes of 5–10 times [2]. The increase in specific activities of naturally occurring radionuclides in combustion products, fly ash and

bottom ash, compared to that of the original coal, depends primarily on the inorganic fraction of the coal.
Therefore, the combustion of coal results in the release of some natural radioactive elements into the environment and in the redistribution of these radioactive elements in the surface soil particularly in the vicinity of coal-fired power plants. This can modify ambient radiation fields and population exposures.
Previously, chemical-physical properties and leaching characteristics of Brazilian coal ashes have been investigated [3] and few studies showed the radioactivity concentration of coal and its combustion residues [1, 4].
Brazilian coals are richer in ash (content of 20–50 wt.%) and poorer in carbon when compared to worldwide coal and coal ash disposal is a serious environmental concern. Only 30% of fly ash is applied as raw material for cement and concrete production. The remaining solid wastes are disposed in on-site ponds, nearby abandoned or active mine sites or landfills. Consequently, the ash piles increases continuously, and this uncontrolled waste disposal site may lead to radiological environmental contamination [3].
An alternative to reduce the environmental impact is the recycling, transforming the coal combustion products into a value added product. The coal ashes can be converted into zeolites due to their high contents of silicon and aluminum. Zeolites synthesized from coal ash are characterized by presenting adsorption properties, catalytic properties and high cation exchange capacity enabling at least 20 applications in various areas of activity. Zeolite synthesis is considered an advanced alternative, because this material is a high value product [5-7].
The classical alkaline conversion of coal ash produces zeolitic material containing mixtures of zeolitic phases and a significant amount of ash of unconverted coal (20-65%). Thus, it is important to monitor whether the utilization of zeolite from coal ash presents a radiation hazard due to the radionuclides that remain in the ash content.
As the release of coal burning byproducts can increase the concentration of radionuclide in the environment, the continuous monitoring is necessary.
The aim of the present study was to determine the radionuclide concentrations in coal, bottom ash, fly ash from cyclone and baghouse filters, zeolites synthesized from the ashes and two different soil samples collected in the vicinity of the power station.

2. MATERIALS AND METHODS

2.1. Materials

All the reagents used for experimental studies were of analytical grade. The samples of coal, fly ash from baghouse filter (FB), fly ash from cyclone filter (FC) and bottom ash (BA) were collected at the Figueira coal-fired power plant located in Paraná State, Brazil. Two soil samples were collected at a distance of 500 m from the coal fired power plant. Soil sample 1 (Soil-1) was in the center of a pasture area and Soil sample 2 (Soil-2) was near the Laranjinha river.

2.2. Synthesis of Zeolites from Coal Ashes

The zeolite was prepared by hydrothermal activation of 20 g of coal ash at 100 °C in 160 mL of 3.5 mol L^{-1} NaOH solution for 24 h. The zeolitic material was repeatedly washed with deionized water to remove excess sodium hydroxide until the washing water had pH ~ 10, then it was dried at 80 °C for 12 h.

2.3. Neutron Activation Analysis

Neutron activation analysis was used to determine the concentrations of the elements U and Th. For this determination, approximately 100 mg of the sample were weighted and packed in polyethylene bags and irradiated in the IEA-R1 nuclear research reactor, at IPEN, in a neutron flux of 1012 n $cm^{-2}s^{-1}$ for a period of 8 hours. Reference materials USGS STM-2, NIST SRM 1646a and a paper filter pipetted with a standard solution of the interest elements were also prepared and irradiated together with the samples to calculate the concentrations by the comparative method.
After the irradiation, two sets of measurement were done. The first, after a one week period of cooling, to determine U concentrations and, the second, after two weeks, to determine Th concentration. Samples were counted for a period of 5000 s, in the first and second measurement, by using an EG&G Ortec Ge high pure Gamma Spectrometer detector (AMETEK Inc., USA) and associated electronics, with a resolution of 0.88 and 1.90 keV for 57Co (122 keV) and 60Co (1332 keV), respectively [8].
Activity concentrations of U and Th were obtained by their specific activity using the conversion factor of 24.5 and 4.05, respectively.

2.4. Gamma Spectrometry

The concentration of the natural radionuclides ^{226}Ra, ^{228}Ra, ^{210}Pb and ^{40}K were carried out by non-destructive γ-ray spectrometry. Samples were packed in 50 cm^3 polypropylene cylindrical containers and they were kept sealed for at least 30 days in order to reach radioactive equilibrium between ^{226}Ra and ^{222}Rn progenies.
A HPGe EG&G Ortec detector with 60% of relative efficiency and 2.09 keV resolution at 1.33 MeV and associated electronic devices were used, with live counting time of 160,000 s. The spectra were acquired by multichannel analyser and, for the analysis, MAESTRO II software package was used. The activity concentration for ^{210}Pb in the samples was corrected for self absorption according to the method described in [9]. The detector efficiency was calibrated by using the reference material IAEA-RGU-1, IAEA-RGTh-1 and IAEA-RGK-1.

3. RESULTS AND DISCUSSION

3.1 Activity Concentrations in Coal and its Combustion Residues

The results obtained for the activity concentration of ^{238}U, ^{226}Ra, ^{210}Pb, ^{228}Ra, ^{232}Th and ^{40}K in the pulverized coal, bottom ash and fly ashes are listed in Table 1. According to UNSCEAR [10], the mean natural radionuclide concentration in coal is 35 Bq kg^{-1} for ^{238}U (range: 16–110), 35 Bq kg^{-1} (range:17–60) for ^{226}Ra, 30 Bq kg^{-1} (range:1–64) for ^{232}Th, and 400 Bq kg^{-1} (range:140–850) for ^{40}K.
As one sees from Table 1, the ^{232}Th and ^{40}K concentrations are in the range of coal reported, and the obtained values for ^{238}U and ^{226}Ra are higher than the UNSCEAR values in coal [10].
The ashes fraction presented concentrations ranging from 683.5 to 1479 Bq kg^{-1} for ^{238}U, from 484 to 1086 Bq kg^{-1} for ^{226}Ra, from 291 to 1891 Bq kg^{-1} for ^{210}Pb, from 67 to 111 Bq $kg^{-1}$for ^{228}Ra, from 80 to 87 Bq kg^{-1} for ^{232}Th and from 489 to 718 Bq kg^{-1} for ^{40}K.

Table 1: Activity concentrations of coal, fly ash from baghouse filter (FB), fly ash from cyclone filter (FC) and bottom ash (BA) (in Bq kg^{-1})

	Coal	BA	FC	FB
^{238}U	216 ± 38	683.5 ± 76	867.5 ± 143	1479 ± 305
^{226}Ra	180 ± 32	484 ± 84	661 ± 115	1086 ± 189
^{210}Pb	<155	291 ± 171	806 ± 300	1891 ± 514
^{228}Ra	27 ± 7	77 ± 24	67 ± 21	111 ± 34
^{232}Th	28 ± 2	83 ± 5	80 ± 5	87 ± 5
^{40}K	192 ± 13	597 ± 39	489 ± 33	718 ± 47

According to standard values published by UNSCEAR [10], the world average concentrations in fly ashes are 240 Bq kg^{-1} for ^{226}Ra, 70 Bq kg^{-1} for ^{232}Th, 265 Bq kg^{-1} for ^{40}K and 200 Bq kg^{-1} for ^{238}U. Comparing the present results, the fly ashes presented higher activity concentration than standard values for all the radionuclides, except for ^{232}Th.
It can be seen that all radionuclide concentration increases from the coal to ash and the highest concentrations were observed in the fly ash from baghouse filter, which has the finest particles [3].
In general, the radionuclide concentrations decreased in the following order FB > FC > BA > coal. The variation of the activity concentration values are due to the differences physical, chemical and geo-chemical properties of materials.
The concentration of the uranium series found in the ashes were lower than the values observed in similar studies carried out 10 years ago and were under the limit adopted by the Brazilian guideline [4, 11].

3.2. Activity Concentrations in Soil Samples

The combustion of coal results in the release of natural radioactive elements into the environment and in the redistribution of these radioactive elements in the surface soil particularly in the vicinity of coal-fired power plants. The Figueira coal-fired power plant has been operating for more than 35 years and only in 1998 was installed a filter system for collecting fly ashes (cyclone and filtering bag–coupled filter system).
Radionuclide (^{238}U, ^{226}Ra, ^{210}Pb, ^{228}Ra, ^{232}Th and ^{40}K) concentrations obtained in the two soil samplings are presented in Table 2. Soil samples collected at about distances of 500 m from the coal-fired power plant had activity concentrations in the range of 28 and 70 Bq kg^{-1}, 23 and 50 Bq kg^{-1}, 199 and 271 Bq kg^{-1}, 22 and 43 Bq kg^{-1}, 23 and 48 Bq kg^{-1}, 237 and 258 Bq kg^{-1} for ^{238}U, ^{226}Ra, ^{210}Pb, ^{228}Ra, ^{232}Th and ^{40}K, respectively.
According to UNSCEAR [10], the current worldwide average values for concentration in soil are 32 Bq kg^{-1} for ^{226}Ra, 45 Bq kg^{-1} for ^{232}Th, 420 Bq kg^{-1} for ^{40}K and 33 Bq kg^{-1} for ^{238}U. Therefore, the activity concentration of ^{238}U is higher than worldwide average concentration for soil samples.

Table 2: Natural radionuclide content in soil samples (in Bq kg^{-1})

	Soil-1	Soil-2
^{238}U	70 ± 12	28 ± 8
^{226}Ra	50 ± 9	23 ± 4
^{210}Pb	199 ± 101	271 ± 128
^{228}Ra	43 ± 13	22 ± 5
^{232}Th	48 ± 3	23 ± 1
^{40}K	237 ± 15	258 ± 17

In general, the radionuclide concentrations of Soil-1 sample were higher than the Soil-2 sample. Lower concentrations were observed for ^{232}Th and ^{228}Ra which were also found in low concentrations in coal and ashes samples.
The obtained concentrations of naturally occurring radionuclides were close to the mean values of the other study with soil samples collect in Figueira coal-fired power plant, with exception of Pb that presented higher values in this work [12].
^{210}Pb is one of the most volatile radionuclide and tends to be enriched on the finer fly ash particles, besides that most ^{222}Rn that migrates into or out of the coal seam, decays to ^{210}Pb because the half time of this radionuclide is short (3.8 days).

3.3. Activity Concentrations in Zeolites Samples

Coal ash as for all materials of mineral origin is a source for natural radioactivity. Recycling coal fly ash can be a good alternative to disposal, and could achieve significant economic and

environmental benefits as well. Hence, it's important to investigate the radiation impact of coal ashes reutilization, mainly about fly ash.
Table 3 presents the values obtained of radioactivity concentrations in zeolites synthesized from: bottom ash (ZBA), fly ash from cyclone filter (ZFC) and fly ash from baghouse filter (ZFB). The results showed that the activity concentrations of the radionuclides present value similar to respective coal ash used as raw material for zeolite synthesis, as can be seen in Table 1.

Table 3: Natural radionuclide content in zeolite from bottom ash (ZBA), zeolite from fly ash from cyclone filter (ZFC) and zeolite from fly ash from baghouse filter (ZFB) (in Bq kg^{-1})

	ZBA	ZFC	ZFB
^{238}U	698 ± 77	849 ± 139	1266 ± 142
^{226}Ra	360 ± 64	370 ± 65	698 ± 124
^{210}Pb	1718 ± 890	3352 ± 1423	2446 ± 1234
^{228}Ra	81 ± 22	87 ± 27	113 ± 28
^{232}Th	85 ± 5	83 ± 5	108 ± 6
^{40}K	<43	344 ± 23	180 ± 1±2

3. CONCLUSIONS

The coal ashes produced in thermal power plants may contain high levels of natural radioactivity and constitute a potential health hazard to the power plant personnel, and to the population living in the vicinity, due to ashes releases, their depositions and their utilization.
The activity concentrations of ^{238}U, ^{226}Ra, ^{210}Pb, ^{228}Ra, ^{232}Th and ^{40}K of coal, coal ash samples (fly ash from baghouse filter, fly ash from cyclone filter and bottom ash) and soil samples collected in the vicinity of the Figueira thermal plant was determined. Radioactive evaluation of all samples showed concentrations above the world average mainly for ^{238}U, because the coal from Figueira is extremely rich in uranium.
Concentrations of radionuclides were relatively high in the coal ashes, and the activity concentrations were higher in the fly ash from baghouse filter than other ashes samples.
The concentration of natural radionuclides presented no significant change when coal ashes were used as starting material for zeolite synthesis.

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