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Natural radioactivity of coal and its by-products in the Baoji coal-fired power plant, China

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Coal, bottom ash and fly ash from the Baoji coal-fired power plant, China were measured for ^{226}Ra, ^{232}Th and ^{40}K by a NaI(Tl) γ-ray spectrometer. The results show that fly ash or bottom ash contain three to six times more natural radionuclides than feed coal. The results are compared with the available data from other countries. Radium equivalent activity and external index are calculated for by-products to assess the radiation hazards arising due to the use of these ash samples in the construction of dwellings. Some fly-ash samples have radium equivalent activities and external hazard index values more than 370 Bq kg^{-1} and unity respectively. The absorbed dose rate at 1 m above the ash pond was (155 nGy h^{-1}) higher than the global average value of 55 nGy h^{-1} and the Chinese average value of 81.5 nGy h^{-1}. The corresponding annual external effective dose is estimated to be 0.191 mSv y^{-1}, which is less than that (0.46 mSv y^{-1}) in areas of natural background radiation.

Keywords: Bottom ash, coal, fly ash, natural radioactivity, γ-spectrometry.

THERE has been an increasing demand for electricity generation throughout the world with the ever-increasing growth in human civilization. With the increasing demand for electricity, coal plays an important role in electric power generation worldwide. China depends largely on coal reserves for energy needs, which contribute more than 70% of the total power generated at present in China[1]. Coal, burned as fuel material in power plants, produces energy and a large amount of solid waste. The solid waste resulting from coal combustion are mainly fly ash and bottom ash. Bottom ash is the coarse-grained material that is collected at the bottom of the boiler and fly ash is entrained in the gas stream and carried up the stack following combustion. Depending on the emission control system of the stack, most of the fly ash is recovered by collection devices and any leftover is released into the atmosphere and deposited on the soil around the coal-fired power plant. The ashes tend to be enriched in inorganic elements (metals and radionuclides).

Since the ashes produced may be either disposed-off or utilized further in other applications such as the building materials industry, it is important to study in detail, the radiological characteristics of the various fractions. Furthermore, detailed knowledge of the radiological characteristics allows better determination of the radiation exposure, both occupational and of the public, due to the produced ashes. Eisenbud and Petro[2] first pointed out that radiation dose from the use of fossil fuel for power generation could be a significant addition to the natural radiation dose. The natural radioactivity of coal and by-products from coal-fired power plant has been noticed in many countries. There are many studies on measurement of concentration of radionuclides in coal and ash or on the estimation of radioactive influence of coal-fired power plant to the ambient environment[3–17], but data for Baoji coal-fired power plant are lacking.

Baoji is the second largest city in the Shaanxi Province in central China. It is located at the western end of the central Shaanxi basin about 150 km west from the provincial capital, Xi'an city. Baoji is surrounded by mountains and plateau in the north, west and south. Only the east is open toward the lower reach of the Weihe River, a major branch of the Yellow River in Shaanxi Province. The Weihe River runs through the city from west to east. Baoji coal-fired power plant with a 60 m stack, situated at the western extremity of the city, has been in operation since 1960s. The power plant with 1.5×10^6 kWh annual production capacity consumes low-quality bituminous coal reserves from Tongchuan of Shaanxi and Huating of Gansu, and produces approximately 4500 tonnes (t) of fly and bottom ash per day from more than 14,000 t of coal. The ash content in the bituminous coal reserve used at the Baoji power plant is in range 12.12–38.82%. There are two big ash ponds (about 1000 m length, 500 m width and 25 m depth) for deposited ash from ash-water. The ash from this power plant is mainly used in producing cement and other building materials or aggregate in stabilizing roadways.

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In this communication, the concentration of ^{226}Ra, ^{232}Th and ^{40}K content of coal, fly ash and bottom ash from the Baoji coal-fired power plant has been estimated using γ-ray spectrometry. Radium equivalent activity, external hazard index of the power plant by-products, used as additives in building materials and natural gamma dose rates 1 m above ash-pond level were calculated. The results obtained in the present study are compared with those of other studies.

Samples of coal, furnace bottom ash and pulverized fly ash were collected from the Baoji coal-fired power plant on a monthly basis during 2005. Twelve coal samples were collected from the coal storage area of the power plant. Twenty-six fly ash samples (12 samples from the bag filter and 14 from the ash pond) and twelve bottom ash samples were sampled from the operating units of power plant respectively. The collected samples were kept in cleaned and numbered polyethylene bags. All coal samples and bottom ash samples were crushed and milled to a fine power with a particle size less than 0.16 mm. Each sample was homogenized and dried in a temperature-controlled furnace at 60°C for 24 h to remove moisture and dry samples (1000 g) were sealed in gas-tight, radon impermeable, trap-shape polyethylene containers (10 cm diameter and 16 cm height, diameter and depth of trap being 6 and 9 cm respectively). These samples were stored for 40 days before counting for radium and thorium daughter products to attain radioactive equilibrium.

The concentration of ^{226}Ra, ^{232}Th and ^{40}K in the samples (1000 g) of coal, fly ash and bottom ash was measured by γ-spectrometry. All radioactivity measurements were performed with a 5 × 5 cm NaI(Tl) scintillation detector with 8% energy resolution (^{137}Cs 661 KeV) and 20 counting efficiency. The detector is maintained in a vertical position in a lead cylindrical shield of 10 cm thickness and 55 cm height. The detector was coupled to a 256 multi-channel pulse height analyser and the system was calibrated for the γ-energy range, 80 keV to 3.2 MeV. The energy regions for ^{40}K (1.46 MeV), ^{226}Ra (1.76 MeV) (Bi-214) and ^{232}Th (2.62 MeV (Tl-208)) were chosen as 1.30–1.60; 1.62–2.00 and 2.45–2.90 MeV respectively. Standard sources for ^{226}Ra and ^{232}Th (in secular equilibrium with ^{228}Th) were prepared using known activity contents and mixing with the matrix material of phthalic acid powder. In order to avoid the loss of gaseous daughter products of ^{226}Ra and ^{232}Th that may lead to disturbance in radioactive equilibrium, the prepared standard sources were kept in sealed, trap-shaped polyethylene containers. Analar grade potassium chloride (KCl) of known amount of the same geometry was used as the standard source of ^{40}K. Samples were counted for about 200 to 400 min. Each weight sample was counted twice before an average was taken.

Data on the concentration of natural radioactivity (^{226}Ra, ^{232}Th and ^{40}K) in the samples of coal, fly ash and bottom ash are presented in Table 1. The results show that the activity concentrations range from 22.9 to 30.4 Bq kg^{-1} for ^{226}Ra, 34.2 to 38.5 Bq kg^{-1} for ^{232}Th and 92.7 to 110.2 Bq kg^{-1} for ^{40}K with an average of 26.3, 36.6 and 99.8 Bq kg^{-1} in coal, from 76.1 to 165.7 Bq kg^{-1} for ^{226}Ra, 118.7 to 195.6 Bq kg^{-1} for ^{232}Th and 261.5 to 520.8 Bq kg^{-1} for ^{40}K with an average of 112.2, 147.5 and 385.6 Bq kg^{-1} in fly ash, and from 63.3 to 110.3 Bq kg^{-1} for ^{226}Ra, 90.5 to 128.2 Bq kg^{-1} for ^{232}Th and 206.5 to 331.8 Bq kg^{-1} for ^{40}K with an average of 93.4, 105.2 and 271.4 Bq kg^{-1} in bottom ash respectively. The results show that in ash produced by the combustion of coal, the concentration of ^{226}Ra is less than that of ^{232}Th. Uranium (parent element of radium) is mainly present in the carbonaceous components of sedimentary rocks and accumulates in coal during the process of coalification. It is mainly present in the organic fraction in coal due to sorptive uptake onto the organic fraction during the early stages of peat-accumulation and burial, whereas thorium is present in the inorganic phases[12]. According to UNSCEAR[18], the mean natural radionuclide concentration 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. The radionuclide concentrations in coal samples from the Baoji power plant are in the range of coal reported in UNSCEAR[18], except for ^{40}K. The reported values of activity concentration of ^{226}Ra, ^{232}Th and ^{40}K in the present study are compared with the finding of other studies (Table 1). The range and average of natural radioactivity concentrations in coal, fly ash and bottom ash from the Baoji thermal power plant are similar to those obtained for the Beijing, Shanghai and Indian thermal power plant samples[14,19,20]. Fly ash or bottom ash from the Baoji coal-fired power plant contains three to six times more ^{226}Ra, ^{232}Th and ^{40}K than that of the feed coal. Coal combustion eliminates organic components causing an increase in radioactivity in ash. However, the enrichment level of natural radionuclides is different between fly ash and bottom ash. During the combustion process, the enrichment level of natural radionuclides in fly ash is higher than that in bottom ash, which is the same as that in other coal-fired power plants[8,16,20,21], whereas the opposite phenomenon is also recorded in a few cases[4,14].

More than 60% fly ash and bottom ash of the Baoji coal-fired power plant is used in producing cement and other building materials or aggregate in stabilizing roadways. The residual ashes are disposed in the ash pond. To assess the radiological hazard of fly ash and bottom ash used as building materials, the radium equivalent activity (Ra_{eq}) and external hazard index (H_{ex}) are used in the study. Ra_{eq} and H_{ex} can be calculated according to Beretka and Mathew[22] as

$$Ra_{eq} = A_{Ra} + 1.43A_{Th} + 0.077A_{K}, \qquad (1)$$

$$H_{ex} = A_{Ra}/370 + A_{Th}/259 + A_{K}/4810, \qquad (2)$$

where A_{Ra}, A_{Th} and A_{K} are the activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K in Bq kg^{-1} respectively. Ra_{eq} is related to

Table 1. Measured natural radioactivity content (Bq kg^{-1}) in coal, fly ash and bottom ash samples from the Baoji coal-fired power plant, P. R. China and comparison with other studies (arithmetic mean values are given in parentheses)

Power plant	Sample	^{226}Ra	^{232}Th	^{40}K
Baoji, China (present study)	Coal	22.9–30.4 (26.3)	34.2–38.5 (36.6)	92.7–110.2 (99.8)
	Fly ash	76.1–165.7 (112.2)	118.7–195.6 (147.5)	261.5–520.8 (385.6)
	Bottom ash	63.3–110.3 (93.4)	90.5–128.2 (105.2)	206.5–331.8 (271.4)
Lodz, Poland[8]	Coal	10.4–28.4	8.5–20.1	43.9–180.3
	Fly ash	54.2–119.3	47.5–91.5	448.5–758.0
	Bottom ash	32.5–90.7	28.4–77.4	307.1–607.2
India[14]	Coal	11.1–66.6 (24.1)	18.5–92.5 (38.5)[a]	14.8–444.1 (82.5)
	Fly ash	40.7–151.7 (77.7)	96.2–177.7 (125.8)[a]	148.0–840.1 (373.8)
	Slag	44.4–155.4 (88.8)	74.0–214.7 (136.9)[a]	373.9–632.9 (377.5)
Kolaghat, India[12]	Coal	25.0–49.9[b]	39.3–55.2	120.8–151[c]
	Fly ash	76.9–117.0[b]	110.5–152.8	72.5–271.8[c]
Hong Kong, China[16]	Coal	17	20	24
	Fly ash	140	155	178
	Bottom ash	100	105	132
Shanghai, China[20]	Coal	29.0–45.5 (36.9)	25.8–45.1 (36.6)	43.3–72.5 (58.9)
	Fly ash	136.5–189.8 (160.3)	123.6–202.4 (159.9)	176.5–278.6 (246.2)
	Bottom ash	78.8–119.9 (114.0)	99.5–133.2 (123.7)	164.3–291.6 (209.4)
Beijing, China[19]	Coal	4.7–58.4 (28.9)	6.6–122 (35.9)	15.7–220 (80.4)
	Fly ash	56.9–160 (101)	50.2–162 (110)	213–699 (347)

[a]Value of ^{228}Ra + ^{228}Th; [b]Value of ^{238}U; [c]Using the conversion factor 3.02×10^{-2} Bq kg^{-1} ppm^{-1}, ^{40}K was calculated.

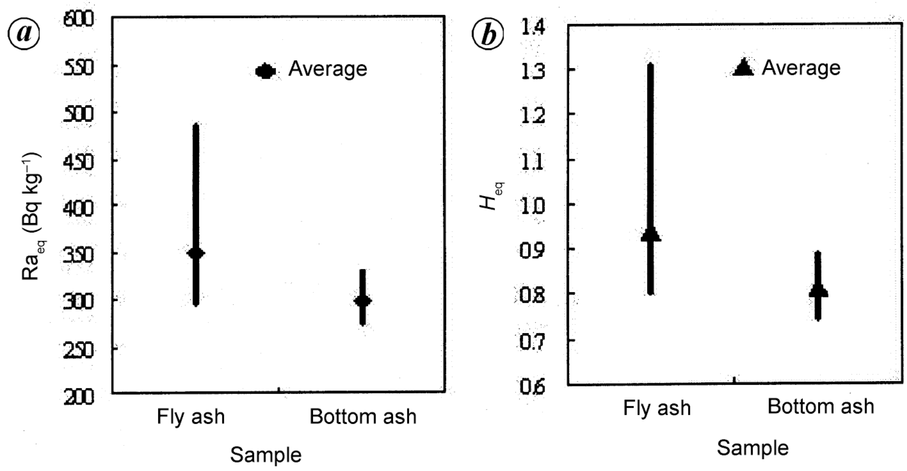

Figure 1. Calculated values of (***a***) Ra_{eq} and (***b***) H_{ex} of fly ash and bottom ash from Baoji coal-fired power plant.

the external γ-dose and internal dose due to radon and its daughters. The maximum value of Ra_{eq} in building materials must be less than 370 Bq kg^{-1} for safe use. H_{ex} is obtained from the Ra_{eq} expression by assuming that its maximum value allowed (equal to unity) corresponds to the upper limit of Ra_{eq} (370 Bq kg^{-1}). The calculated values of Ra_{eq} range from 296.1 to 485.5 Bq kg^{-1} with average of 349.6 Bq kg^{-1} for fly ash, and from 274.3 to 330.2 Bq kg^{-1} with average of 298.3 Bq kg^{-1} for bottom ash (Figure 1 *a*). Ra_{eq} values of six fly-ash samples are more than 370 Bq kg^{-1}. The calculated values of H_{ex} range from 0.80 to 1.31 with an average of 0.94 for fly ash, and from 0.74 to 0.89 with average of 0.81 for bottom ash (Figure 1 *b*). The H_{ex} values of six fly-ash samples are more than one. Thus when fly ash is used as building material, it is important to assess its radiation potential[23]. The average relative contribution to Ra_{eq} and H_{ex} due to ^{226}Ra, ^{232}Th and ^{40}K is 31, 61 and 8% for fly ash, and 32, 60 and 8% for bottom ash respectively. Thus the main contributions to radium equivalent activity and external hazard index are ^{232}Th and ^{226}Ra for fly ash and bottom ash.

An attempt has been made in the present study to evaluate the gamma dose emitted from the ash pond. Conversion factors to transform specific activities A_K, A_{Ra} and A_{Th} of K, Ra and Th respectively, in absorbed dose rate at 1 m above the ground (in nGy h^{-1} by Bq kg^{-1}) are calculated by Monte Carlo method and the values are[18]

$$D(\text{nGy h}^{-1}) = 0.0417A_K + 0.462A_{Ra} + 0.604A_{Th}. \quad (3)$$

The calculated results show that the absorbed dose rates range from 118 to 216 nGy h^{-1} with mean value of 155 nGy h^{-1} for ash samples from the ash pond. All the calculated dose rates were higher than the global average value (55 nGy h^{-1})[24] and the Chinese average value (81.5 nGy h^{-1})[25]. In order to estimate the annual effective dose rates, the conversion coefficient from the absorbed dose in air to the effective dose (0.7 Sv Gy^{-1}) and the outdoor occupancy factor (0.2) proposed by UNSCEAR[18] were used. The effective dose rate was calculated using the formula:

$$\text{Effective dose rate (mSv y}^{-1}) = D(\text{nGy h}^{-1}) \times 8760\ (\text{h y}^{-1}) \times 0.2 \times 0.7\ (\text{Sv Gy}^{-1}) \times 10^{-6}. \quad (4)$$

The calculated effective dose rates in air varied from 0.144 to 0.265 mSv y^{-1}, with an average value of 0.191 mSv y^{-1}. In areas with normal background radiation, the average annual external effective dose rate from the terrestrial radionuclides is (0.46 mSv y^{-1})[26,27]. The obtained values of natural radioactivity and γ-absorbed dose rates in air, thus demonstrate that the Baoji ash pond is an area with normal natural background radiation.

Gamma-ray spectrometric study shows that fly ash and bottom ash from the Baoji coal-fired power plant, China have three to six times more natural radionuclides than that of feed coal. During the combustion process, the enrichment level of natural radionuclides in fly ash is higher than that in bottom ash. Radium equivalent activity (Ra_{eq}) and external hazard index (H_{ex}) values of six fly ash samples are more than 370 Bq kg^{-1} and unity respectively. The main contributions to radium equivalent activity and external hazard index are ^{232}Th and ^{226}Ra for fly ash and bottom ash, and hence when these are used as additives in building materials, the concentration of natural radionuclides should be monitored. The calculated absorbed dose rate at 1 m above the ground was 155 nGy h^{-1}, which is higher than the global average value of 55 nGy h^{-1} and the Chinese average value of 81.5 nGy h^{-1}. However, the average external effective dose rate in the ash pond is 0.191 mSv y^{-1}, which is lower than the average annual external effective dose rate (0.46 mSv y^{-1}) from the terrestrial radionuclides. The study thus shows that the Baoji ash pond is an area with normal natural background radiation.

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