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Enrichment and particle size dependence of polonium and other naturally occurring radionuclides in coal ash

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ABSTRACT

Coal fired thermal power contributes 70% of power in India. Coal fired power generation results in huge amounts of fly ash and bottom ash of varying properties. Coal, which contains the naturally occurring radionuclides, on burning results in enrichment of these radionuclides in the ashes. In the present study, coal, bottom ash and fly ash samples collected from six coal-fired power plants in India were measured for ^{210}Po using alpha spectrometry and for natural U, ^{226}Ra, ^{232}Th and ^{40}K by an HPGe γ-ray spectrometer. ^{210}Po in fly ash ranged from 25.7 to 70 Bq/kg with a mean value of 40.5 Bq/kg. The range and mean activities of ^{238}U, ^{226}Ra, ^{232}Th, ^{40}K in fly ash were 38.5–101 (78.1), 60–105.7 (79), 20–125 (61.7) and 43.6–200 (100) Bq/kg respectively. Fly ash and bottom ash contains two to five times more natural radionuclides than feed coal. The results were compared with the available data from earlier studies in other countries. The effect of particle size on enrichment factor of the nuclides in fly ash was studied. ^{210}Po showed the largest size dependence with its concentration favoring the smaller particle size while ^{232}Th showed least size dependence. ^{238}U and ^{226}Ra showed behavior intermediate to that of ^{210}Po and ^{232}Th. Also the correlation between sulfur content of the feed coal and activity of ^{210}Po was investigated. Increased sulfur content in feed coal enhanced enrichment of ^{210}Po in ash.

1. Introduction

Coal is the largest source of energy for the generation of electricity worldwide. Nearly 40% of the electricity generated globally is derived from the combustion of coal while 17% is contributed by nuclear power. The first electric company started in 1880 and a coal-fired boiler connected to a steam engine and dynamo came into operation in 1882 (State of the World, 1994). In developing countries like India, coal has a significant role in power generation. The rapid increase in thermal generation capacity and at the same time a deterioration of the quality of coal used has resulted in increased generation of fly ash and bottom ash of varying properties. Indian coal generally has high ash content (35–45%) and is of lower quality (Mathur et al., 2003; Bhangare et al., 2011). The fly ash and bottom ash generated from coal fired thermal power plants are significant sources of exposure for the population in the vicinity of the plant to naturally occurring radionuclides (Zeevaert et al., 2006; Sahu et al., 2009).

Coal contains trace amounts of natural radionuclides and their daughter products which discharge to the atmosphere during combustion. The quantity of radionuclides emitted to the atmosphere depends on the concentration in the coal, the method of combustion and the efficiency of the fly ash recovery. Over the years there has been growing concern on the radioactivity in coal and its ashes. A large number of studies have been carried out worldwide for evaluating the radioactivity releases from coal and its products (Papastefanou, 1996; Niewiadomski et al., 1986; Mishra, 2004; Tadmor, 1986; McBride et al., 1978). There are two pathways for release of radioactivity in the environment due to combustion of coal. The volatile gases and semi volatile elements are released to the atmosphere. It is assumed that 100% of the radon, 10% of the lead and polonium, and 1% of the other radionuclides in coal are released into the atmosphere (Corbett, 1983). The non-volatile nuclides are enriched and concentrated in the ashes. Some of the fly ash particles which are lighter and smaller, are expelled with hot gases and a fraction of nuclides goes with these solid phase/smoke particles. The world arithmetic averages of activity mass concentrations in escaping fly ash are 265 Bq/kg for ^{40}K, 200 Bq/kg for ^{238}U, 240 Bq/kg for ^{226}Ra, 930 Bq/kg for ^{210}Pb, 1700 Bq/kg for ^{210}Po, 70 Bq/kg for

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^{232}Th, 110 Bq/kg for ^{228}Th and 130 Bq/kg for ^{226}Ra (UNSCEAR, 1988).

The activity in ashes depends on various physico-chemical properties of coal along with the power plant conditions. It is also well known that the specific activity in the fly ash increases with decreasing particle size, so the escaping ash which is the finest fraction has a higher concentration than the fly ash captured in the filters (Papastefanou and Charalambous, 1984; Roeck et al., 1987). During coal combustion, the elements in minerals and organic fractions of coal are liberated and distributed into combustion products, i.e. bottom ash, fly ash and flue gas (Tang et al., 2012). The distribution patterns of these elements in combustion products depend largely on the volatility and occurrence of elements in coal, and the operational parameters and air pollution control devices deployment of the combustion boilers (Clarke, 1993; Miller et al., 2002). Bottom ash is supposed to enrich in inert elements, whereas the fly ash, captured by electrostatic precipitator (ESP) enrich preferentially in volatile elements (Liu et al., 2004). The enrichment factors of certain elements can sometimes reach to a few fold or even several magnitudes, relative to the feed coals (Bhattacharyya et al., 2009). In addition, large portions of volatile elements are possibly emitted to the atmosphere through generated flue gases in stack.

Naturally occurring radionuclides such as ^{210}Po, ^{226}Ra, ^{238}U, ^{232}Th and ^{40}K released by the power plant pose a potential health hazard (Mishra, 2004). More importantly, ^{210}Po is a potential health hazard owing to its short half-life and the highly energetic cell disrupting alpha particles (5.3 MeV) emitted during its decay process. Besides, once ^{210}Po in the air is assimilated into the flora and fauna, it may be bio-concentrated in the food chain and, thus, pose further threat to human health (Daish et al., 2005). Polonium is volatile and will condense preferably on finer ash particles, against which the electro filters are less effective. Measurements reported by Coles et al. (1978) and Tadmor (1986) indicate a discharge of polonium particles being 2–4 times higher than those of uranium and radium. It is evident that the distribution of elements adsorbed on fly ash particles depends on the size of fly ash particles along with the factors like boiler temperature, ash content, physico-chemical characteristics of feed coal. The concentration of elements in fly ash depends largely on the size fractions of the escaping fly ash (Bhangare et al., 2011).

There are numerous studies on the co-chemistry of sulfur and polonium in the bio-organic matrices, however in an organic matrix like coal where the polonium concentrations are important from the radiological safety point of view, very few or no studies have been reported in the literature. Polonium which is influenced by the sulfur cycle and the sulfur bacteria, is studied in various systems including aquatic and biological systems (Harada et al., 1989; Cherrier et al., 1995; Stewart et al., 2008) but there has been no much attempts on its chemistry with sulfur in an organic mineral like coal. However because the coal is an organic mineral and contains significant amounts of both sulfur and polonium, the dependence of polonium concentration on sulfur content in the coal can be studied and the correlation between both the elements can be established.

In the present study, fly ash samples collected from six coal-fired power plants across India were measured for ^{238}U, ^{226}Ra, ^{232}Th and ^{40}K by an HPGe γ-ray spectrometer, while ^{210}Po was radiochemically extracted and counted by alpha spectrometer. The dependence of activity concentration of individual radionuclides on size of the fly ash particles was studied and the correlation of sulfur content in coal to the activity concentration of ^{210}Po in fly ash also was studied.

2. Materials and methods

2.1. Sample collection

The feed coal at all power stations was sampled on 5 different days (once every week) over a period of one month. This one month period of sampling assured that the samples obtained were truly representing the feed coal at each plant, since the coal samples at individual power stations are obtained from single mine only. About 2–3 kg of sample was obtained in duplicates from samplers located at the coal feeder of the boilers. This gave the representative sample of the coal that was fed to the boilers after powdering and washing etc. The two samples during each sampling were further homogenized to obtain a gross sample. The fly ash and bottom ash samples from the 6 power stations were also sampled in parallel (about 10 samples of each from individual power stations). Bottom ash samples were collected from the ashers of the boiler and fly ash from the hoppers of the electrostatic precipitators. The efficiency of the electrostatic precipitators was as high as 99% in all the plants. The gross samples were further air-dried, milled, and split carefully in accordance with ISO recommendations to obtain a representative subsample of particle size <250 μm for further chemical analyses. The fly ash samples were also fractionated into 4 sizes (2 μm, 4 μm, 6 μm and 18 μm) with the help of an electromagnetic sieve shaker in order to check the dependence of radionuclide concentration on the size of the fly ash particles. Most of the power stations under study use Indian coal as the feed material. The location details of individual power plants along with the generation capacity are shown in Fig. 1.

2.2. Samples processing

The samples were processed by two pathways. One part was processed for analysis of ^{210}Po in it by alpha spectrometry, whereas the other part was processed for estimation of other radionuclides by gamma spectrometry.

For gamma spectrometry, the samples were dried for 24 h in an air-circulation oven at 110 °C. Samples were further powdered; homogenized and about 100 g of each sample was filled in plastic containers of 6.5 cm diameter × 7.5 cm height and sealed to make them airtight for 6 months. This provided the longest-lived intermediary radionuclide ^{234}Th (24.1days) the opportunity to come to within 1% of secular equilibration with its parent ^{238}U. After attainment of secular equilibrium the samples were subjected to gamma-ray spectrometric analysis.

For ^{210}Po, about 5 g of fly ash sample was digested first with HNO_3 and 4 N HCl sequentially. The acids were evaporated to near dryness and made up to 80 mL by adding 1 N HCl with ascorbic acid to reduce interfering Fe(III). Tracer activity 3.0Bq/ml including ^{209}Po was added to the aliquots. Then silver planchets were submerged into the solutions and were kept at a temperature of about 85 °C for 7 h with continuous stirring. The planchets thereafter were dried under infra-red lamp and alpha activities were determined in alpha spectrometer.

2.3. Alpha spectrometric analysis

Samples were counted in an eight-chamber integrated alpha spectrometry system equipped with ion-implanted Si-charged-particle detectors, with an active detector-surface area of 450 mm^2, and a source-to-detector distance of approximately 10 mm. Samples and blanks were counted for nominally 250,000 s. Background measurements were made immediately prior to the measurements.

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