Radon activity and exhalation rates in Indian fly ash samples

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Fly ash is the by-product of burnt coal which is naturally occurring radioactive material (NORM). Because of human activity and its use in manufacturing of bricks, sheets, cement, land filling etc may present a radiation hazard to people and the environment Thus, it is very important to carry out radioactivity measurements in fly ash from the health and hygiene point of view. In the present study, the activity concentrations of $^{238}$U, $^{232}$Th and $^{40}$K have been varied from 99 ± 2 to 203 ± 4 Bq/kg, 145 ± 2 to 288 ± 4 Bq/kg, and 355 ± 5 to 516 ± 6 Bq/kg, respectively in various fly ash samples The radium equivalent activity was varied from 317 to 614 Bq/kg, radon activity varied from 214 to 590 Bq/m$^3$, radon exhalation rate varied from 7.8 to 21.6 mBqkg$^{-1}$h$^{-1}$ for mass exhalation rate and from 138 to 381 mBq$m^{-2}$h$^{-1}$ for surface exhalation rate in the fly ash samples used in the present investigation. The absorbed dose varied from 143 to 277 mGy, the indoor annual effective dose varied from 0.70 to 1.36 mSv and the outdoor annual effective dose varied from 0.17 to 0.34 mSv In all the samples, the activity concentration of $^{238}$U, $^{232}$Th and $^{40}$K was found to be below the permissible levels. A strong positive correlation has been observed between uranium concentration, radon activity and radon exhalation rate.

Keywords: Radon, Uranium, Thorium, Radium, Health, Environment, Coal, Fly ash, Exhalation rate

1 Introduction

Measurements of radioactivity in technologically enhanced naturally occurring radioactive materials (TENORMs) are important from radiation protection point of view because more than 50% of the total dose to human population from natural sources of radiation is contributed by these materials. The main contribution is due to inhalation of $^{222}$Rn (radon), $^{220}$Rn (thoron) and their progeny which are the most important radioactive and potentially hazardous elements emitted by primordial radionuclides present in (TENORMs) and are released in the environment. Fly ash is technologically important material generated during burning of coal and is used in manufacturing of bricks, sheets, cement, land filling etc. Natural radioactivity in fly ash comes from $^{238}$U and $^{232}$Th series and natural $^{40}$K and the increased interest in measuring radioactivity in terms of activity concentration of $^{238}$U, $^{232}$Th and $^{40}$K, radon concentration and radon exhalation rate in fly ash is due to its health hazards and environmental pollution. It has been reported that the combustion of coal in various thermal power plants results in the release of some natural radioactivity to the environment and the greatest part of the coal radioactivity remains with the ashes. Fly ash is a potential carcinogen containing heavy metals, hazardous organic compounds, and $^{226}$Ra which decays to form chemically inert radioactive gas $^{222}$Rn. Concentration of radionuclides in cinder (fly ash) grows 3-4 times as compared with the original matter and this results in a heavy contamination of the environment and causes problems with the removal of such ash. When used in building construction materials (bricks, cement etc.) it becomes potentially hazardous. Radon concentration has been reported higher in a house with fly ash than in a house built without it.

The radionuclides concentration evaluation in the samples with respect to the natural background levels and regulatory control actions, estimating the
potential environmental transport to man, and studying the magnitude and extent of deposition, especially for long-term releases, are very good reasons to carry out a radiological characterization of fly ash and to select that which contains the lowest amount of harmful matters. In the present paper, samples of fly ash from different thermal power stations in northern India and various fly ash using establishments were collected and analyzed for the activity concentration of the natural radionuclides namely $^{238}$U, $^{232}$Th and $^{40}$K using gamma spectrometry system. The detector is a co-axial $n$-type high-purity germanium detector (Make EG&G, ORTEC, Oak Ridge, USA). The detector has a resolution of 2.0 keV at 1332 keV and relative efficiency of 20%. The output of the detector is analyzed using a 4K ADC system connected to PC, the spectrum is analyzed using the locally developed software "CANDLE (Collection and Analysis of Nuclear Data using Linux nEtwork)". The detector is shielded using 4" lead on all sides to reduce the background level of the system. The efficiency calibration for the system is carried out using secondary standard source of uranium ore in geometry available for the sample counting. Efficiency values are plotted against energy for particular geometry and fitted by least squares method to an empirical relation that takes care of the nature of efficiency curve for the HPGe detector. The samples were counted for a period of 72000 seconds and the spectra are analyzed for the photo peak of uranium, thorium and radium. The net count rate under the most prominent photo peaks of radium and thorium daughter peaks is calculated by subtracting the respective count rate from the background spectrum obtained for the same counting time. Then, the activity of the radionuclides is calculated from the background subtracted area of prominent gamma ray peaks.

2 Experimental Details

2.1 Radiometric studies (measuring activity concentration of uranium, thorium and potassium)

The fly ash samples were collected from different thermal power stations in northern India and various fly ash using establishments. After collection, about 300 gm of each sample was crushed into fine powder by using Mortar and Pestle. Fine quality of the sample was obtained using plastic sieve of 150 micron-mesh size. Before measurement, samples were dried in an oven at about 110°C for 24 hr. Each sample was packed and sealed in an airtight PVC container and kept for about 4 week period to allow radioactive equilibrium between $^{226}$Ra and the radon ($^{222}$Rn) and their short lived decay products. About 250-300 g of sample in powder form was taken for each material. For calibration of the low background counting system a secondary standard was obtained, which was calibrated with the primary standard obtained from the International Atomic Energy Agency Gamma transitions of 186 keV for $^{220}$Ra, 295 and 352 keV for $^{214}$Pb, 609, 1120 and 1764 keV for $^{214}$Bi, 338, 463, 911 and 968 keV for $^{228}$Ac, 727 keV for $^{212}$Bi, 238 keV for $^{212}$Pb were used for the laboratory measurement of activity concentration.

Using HPGe detector of high-resolution gamma spectrometry system, the activity in the samples was measured. The detector is a co-axial $n$-type high-purity germanium detector (Make EG&G, ORTEC, Oak Ridge, USA). The detector has a resolution of 2.0 keV at 1332 keV and relative efficiency of 20%. The output of the detector is analyzed using a 4K ADC system connected to PC, the spectrum is analyzed using the locally developed software “CANDLE (Collection and Analysis of Nuclear Data using Linux nEtwork)”. The detector is shielded using 4" lead on all sides to reduce the background level of the system. The efficiency calibration for the system is carried out using secondary standard source of uranium ore in geometry available for the sample counting. Efficiency values are plotted against energy for particular geometry and fitted by least squares method to an empirical relation that takes care of the nature of efficiency curve for the HPGe detector. The samples were counted for a period of 72000 seconds and the spectra are analyzed for the photo peak of uranium, thorium and radium. The net count rate under the most prominent photo peaks of radium and thorium daughter peaks is calculated by subtracting the respective count rate from the background spectrum obtained for the same counting time. Then, the activity of the radionuclides is calculated from the background subtracted area of prominent gamma ray peaks.

2.2 Measuring radon concentration and radon exhalation rates from soil samples

For radon concentration and exhalation rate measurements from the samples, ‘Can Technique’ was used. 150 µm grain size samples, each of mass 100 g was kept in plastic cylindrical cans of 10 cm height and 7 cm diameter. The LR-115 plastic track detector was fixed on the bottom of the lid of each can with cello tape. The can is tightly closed from the top and sealed such that the sensitive side of the detector always faced the specimen and is exposed freely to the emergent radon from the sample in the can so that it could record alpha particles resulting from the decay of radon in the remaining volume of the can and from $^{218}$Po and $^{214}$Po deposited on the inner walls of the can. Radon and its daughters reach equilibrium with $^{226}$Ra in about 4 weeks and hence the equilibrium activity of emergent radon could be obtained from the geometry of the can and time of the exposure. Following the exposure for a stipulated period (about 90 days), the LR-115 films (SSNTDs) were chemically etched in 2.5 N NaOH (sodium hydroxide) solution in an etching bath with a magnetic stirrer at a temperature of 60°C±1°C for a period of 75 min for developing the tracks recorded and registered in the films. The etching process removed a bulk thickness of about 4 µm leaving a residual detector thickness of about 8 µm. The stirring was done as per the standard prescribed and a stabilized power supply with online UPS was used to control the stirring. The temperature and the time of etching were controlled so that required thickness of active layer is maintained. The detectors are then washed in triple distilled water and
deionized water in succession. During washing, Teflon coated long tweezers are used to handle these detectors. The detectors having a residual thickness of 8µm after etching are peeled off from their plastic bases and the registered tracks of alpha particles can be counted by using spark counter. The spark counter is pre-sparked at a voltage of 900 V and is operated at 450 V. Its design characteristics are similar to the one discussed by Garakani.

3 Results and Discussion

3.1 Estimation of uranium, thorium and potassium in various samples

The concentrations of uranium, thorium and potassium were calculated using the following equation:

\[
\text{Activity (Bq)} = \frac{CPS \times 100 \times 100 + CPS_{\text{true}} \times 100 \times 100}{B.I. \times \text{Eff}} \times \frac{B.I. \times \text{Eff}}{B.I. \times \text{Eff}}
\]

where, \( CPS \) is net count rate per second; \( B.I. \) the Branching Intensity, and \( \text{Eff} \) is efficiency of the detector.

Table 1 presents the average concentration of the radionuclides, \( ^{238}\text{U} \), \( ^{232}\text{Th} \), and \( ^{40}\text{K} \), as well as the corresponding standard deviation in the materials under investigation. The activity concentration for \( ^{238}\text{U} \), \( ^{232}\text{Th} \), and \( ^{40}\text{K} \) varies from 99 ± 2 to 203 ± 4 Bq/kg, 145 ± 2 to 288 ± 4 Bq/kg, and 355 ± 5 to 516 ± 6 Bq/kg, respectively in various samples studied in the present work. From Table 1, it is clear that the average concentration of the radionuclide \( ^{40}\text{K} \) is below the detection limit in more than 50% of the samples.

3.2 Estimation of absorbed and effective dose

The measured activity concentrations of \( ^{238}\text{U} \), \( ^{232}\text{Th} \), and \( ^{40}\text{K} \) were converted into doses (nGy h\(^{-1}\) per Bq kg\(^{-1}\)) by applying the factors 0.462, 0.604 and 0.0417 for uranium, thorium and potassium, respectively. These factors were used to calculate the total absorbed gamma dose rate in air at one meter above the ground level using the following equation:

\[
\text{Absorbed dose } D(\text{nGy h}^{-1}) = 0.462C_U + 0.604C_{\text{Th}} + 0.0417C_K \quad \ldots(2)
\]

where \( C_U \), \( C_{\text{Th}} \), and \( C_K \) are the activity concentrations (Bq/kg) of uranium, thorium and potassium in the samples. To estimate annual effective doses, account must be taken of (a) the conversion coefficient from absorbed dose in air to effective dose and (b) the indoor occupancy factor. Annual estimated average effective dose equivalent received by a member is calculated using a conversion factor of 0.7 Sv Gy\(^{-1}\), which is used to convert the absorbed rate to annual effective dose with an outdoor occupancy of 20% and 80% for indoors. The annual effective doses are determined as follows:

Indoor (mSv) = (Absorbed Dose) \( n\text{Gy h}^{-1} \times 8670\text{h} \times 0.8 \times 0.7\text{Sv Gy}^{-1} \)

\ldots(3)

Outdoor (mSv) = (Absorbed Dose) \( n\text{Gy h}^{-1} \times 8670\text{h} \times 0.2 \times 0.7\text{Sv Gy}^{-1} \)

\ldots(4)

Using Eqs (2)-(4), the absorbed and annual effective dose rates from the samples were calculated as presented in Table 2. For realistic situation, the studies in houses made up of fly ash bricks were carried out and the results have been published. The minimum and maximum values of absorbed dose, indoor annual effective dose and outdoor annual effective dose are presented in Table 2.

<table>
<thead>
<tr>
<th>Sr No</th>
<th>Sample code</th>
<th>Activity concentration (Bq/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>( ^{238}\text{U} )</td>
</tr>
<tr>
<td>1</td>
<td>FA-1</td>
<td>202 ± 2</td>
</tr>
<tr>
<td>2</td>
<td>FA-2</td>
<td>164 ± 3</td>
</tr>
<tr>
<td>3</td>
<td>FA-3</td>
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<td>149 ± 2</td>
</tr>
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<td>FA-5</td>
<td>158 ± 3</td>
</tr>
<tr>
<td>6</td>
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<td>114 ± 2</td>
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<td>FA-7</td>
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<td>99 ± 2</td>
</tr>
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<td>11</td>
<td>FA-11</td>
<td>179 ± 4</td>
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</table>

BDL — Below Detection Limit

<table>
<thead>
<tr>
<th>Sr No</th>
<th>Sample code</th>
<th>Absorbed dose (nGy h(^{-1}))</th>
<th>Annual effective dose, (mSv)</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td>Indoor</td>
<td>Outdoor</td>
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<td>277</td>
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<tr>
<td>2</td>
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<td>219</td>
<td>1.08</td>
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<td>FA-3</td>
<td>183</td>
<td>0.90</td>
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<tr>
<td>4</td>
<td>FA-4</td>
<td>217</td>
<td>1.07</td>
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<tr>
<td>5</td>
<td>FA-5</td>
<td>224</td>
<td>1.10</td>
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<td>6</td>
<td>FA-6</td>
<td>152</td>
<td>0.75</td>
</tr>
<tr>
<td>7</td>
<td>FA-7</td>
<td>143</td>
<td>0.70</td>
</tr>
<tr>
<td>8</td>
<td>FA-8</td>
<td>192</td>
<td>0.94</td>
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<tr>
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<td>253</td>
<td>1.24</td>
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<td>FA-10</td>
<td>166</td>
<td>0.81</td>
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<tr>
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<td>FA-11</td>
<td>226</td>
<td>1.11</td>
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effective dose were found to vary from 143 to 277 nGy h\(^{-1}\), from 0.70 to 1.36 mSv and from 0.17 to 0.34 mSv, respectively in various samples under investigation. In some of the samples, the absorbed dose and indoor annual effective dose from the fly ash samples was more than the recommended safety limit of 1 mSv/y for the general public\(^{17}\). The present case gives the dose from fly ash directly. In practice, when fly ash is mixed with other materials then levels are enhanced as per the percentage of fly ash used. For realistic situation, the dose will be smaller and depend upon the percentage of fly ash used. The positive correlation was observed between the uranium activity and the absorbed dose.

3.3 Radon concentration and radon exhalation rate measurements

The radon activity or integrated radon exposure\(^{10,18,19}\) inside the can was obtained by using the calibration factor 0.056 tracks cm\(^{-2}\) day\(^{-1}\)=1 Bq m\(^{-3}\)

Exhalation rates \((E_x)\) were calculated using the Eqs (5 and 6) used by various researchers\(^{18,19}\):

For mass exhalation rate:

\[
E_x = \frac{CV\lambda}{T + 1/\lambda(e^{-\lambda T} - 1)}(\text{Bq kg}^{-1} \text{h}^{-1}) \quad \ldots (5)
\]

and for surface exhalation rate:

\[
E_s = \frac{CV\lambda}{T + 1/\lambda(e^{-\lambda T} - 1)}(\text{Bq m}^{-2} \text{h}^{-1}) \quad \ldots (6)
\]

where \(C\) is the integrated radon exposure (Bq m\(^3\) h\(^{-1}\)); \(V\) the volume of air in can (m\(^3\)); \(T\) the time of exposure (hrs); \(\lambda\) the decay constant for radon (h\(^{-1}\)); \(A\) is the area covered by the can or surface area of the sample (m\(^2\)).

The radium equivalent activity was calculated using Eq. (7).

\[
Ra_{eq}(\text{Bq kg}^{-1}) = (C_U + 1.43 C_{Th} + 0.077 C_K) \quad \ldots (7)
\]

where \(C_U\), \(C_{Th}\), and \(C_K\) are the activity concentrations (Bq/kg) of uranium, thorium and potassium in the samples\(^{20}\).

The calculated values are presented in Table 3. The radium equivalent activity was varied from 317 to 614 Bq/kg, radon activity from 214 to 590 Bq/m\(^3\), radon exhalation rate from 7.8 to 21.6 mBq kg\(^{-1}\) h\(^{-1}\) for mass exhalation rate and from 138 to 381 mBq m\(^{-2}\) h\(^{-1}\) for surface exhalation rate in the fly ash samples used. The values recorded in present investigation are found to be in good agreement with the results reported by other researchers\(^{21-26}\), for fly ash and for other building materials\(^{24,27-29}\).

The results indicate that the values for fly ash samples are higher than the corresponding values for other building materials. The findings clearly indicate that the addition of fly ash in other building materials augments the activity and may present a radiation hazard to people and the environment. The radon activity and exhalation rates are found to vary appreciably in various samples. It is due to the fact that the samples collected from different thermal power stations were supplied from different collieries. The variation may be due to the differences in the radium content\(^{30,31}\) and porosity\(^{32}\). The graph for the correlation between radon activity and exhalation

<table>
<thead>
<tr>
<th>Sr No</th>
<th>Sample code</th>
<th>Radon activity (Bq/m(^3))</th>
<th>Radium equivalent activity (Ra_{eq}) (Bq/kg)</th>
<th>Mass exhalation rate (mBq kg(^{-1}) h(^{-1}))</th>
<th>Surface exhalation rate (mBq m(^{-2}) h(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>FA-1</td>
<td>590</td>
<td>614</td>
<td>21.6 ± 1.8</td>
<td>381 ± 31.1</td>
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<tr>
<td>2</td>
<td>FA-2</td>
<td>443</td>
<td>479</td>
<td>17.2 ± 1.4</td>
<td>304 ± 24.8</td>
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<tr>
<td>3</td>
<td>FA-3</td>
<td>295</td>
<td>485</td>
<td>13.0 ± 0.9</td>
<td>228 ± 16.1</td>
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<tr>
<td>4</td>
<td>FA-4</td>
<td>413</td>
<td>481</td>
<td>16.2 ± 1.3</td>
<td>286 ± 23.3</td>
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<tr>
<td>5</td>
<td>FA-5</td>
<td>472</td>
<td>496</td>
<td>17.3 ± 1.4</td>
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<tr>
<td>6</td>
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<td>266</td>
<td>337</td>
<td>9.8 ± 0.7</td>
<td>171 ± 12.1</td>
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<td>7</td>
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<td>214</td>
<td>317</td>
<td>7.8 ± 0.5</td>
<td>138 ± 9.7</td>
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<td>512</td>
<td>561</td>
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<td>360</td>
<td>10.8 ± 0.8</td>
<td>190 ± 13.4</td>
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<tr>
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<td>FA-11</td>
<td>498</td>
<td>502</td>
<td>19.5 ± 1.6</td>
<td>346 ± 28.2</td>
</tr>
</tbody>
</table>

Mass of the sample (M) = 0.10 kg; Height of the sample (h) = 1.8 cm; Surface area of the sample (A) = 45.4×10\(^{-4}\) m\(^2\); Volume of air in the can (V) = 368×10\(^{-6}\) m\(^3\).

Fig. 1 — Variation of surface exhalation rate with radon activity
rates is shown in Figs 1 and 2. A strong correlation coefficient was observed between radon activity, mass and surface exhalation rate with a correlation coefficient of $R^2 = 0.96$ and 0.97, respectively. The strong correlation between radon activity and radon exhalation rate suggests the significant contribution of fly ash towards indoor radon. Overall positive correlation was seen between $^{238}\text{U}$ activity concentration, radium equivalent activity and exhalation rates.

4 Conclusions

The present investigation shows that the building construction materials which have been technologically enhanced to be used for construction purpose do have inborn radioactivity in them due to presence of primordial radionuclides and the radioactivity is modified in these materials during technological enhancement. The presence of natural radioactivity levels in the fly ash samples analysed in the present study is well below the acceptable limits. The activity concentration, absorbed dose and annual effective dose is marginally higher as compared to the other building materials. However, these materials satisfy the universal standards limiting the radioactivity within the safe limits of 1000, 1000 and 4000 Bq/kg for $^{238}\text{U}$, $^{232}\text{Th}$ and $^{40}\text{K}$, respectively. In more than 50% of the fly ash samples, the dose equivalents found are slightly more than the safe limit of 1 mSv/y for indoor. From this study, it is quite clear that the dose equivalent received by the public in large and the workers in particular is slightly more than the recommended safety limits. In the light of these findings, the users and promoters of use of fly ash in concrete, Portland Pozzolona cement etc must take a serious view of the problem. From the radiological point of view, the use of fly ash as building material, may affect indoor doses from external irradiation. The inhalation of radon decay products may increase significantly.

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