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Analysis of Natural Radioactivity in Coal and Ashes from a Coal Fired Power Plant

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Coal is widely used mineral due to its accessibility and abundance in nature. Coal contains naturally occurring radionuclides or Natural Occurring Radioactive Materials (NORM) from Uranium and Thorium series including their decayed daughters namely Uranium-238 (^{238}U), Radium-226 (^{226}Ra) and Thorium-232 (^{232}Th) along with Potassium-40 (^{40}K). These radionuclides which are a natural phenomenon are released to the environment and concentrated in the ashes resulting from the combustion process. This paper presents an evaluation of the radioactivity content found in the feed coal (FC), bottom ash (BA) and fly ash (FA) sampled from a typical coal fired power plant (CFPP). The samples were measured for activity concentration of several radionuclides namely ^{238}U, ^{226}Ra, ^{232}Th and ^{40}K by using Instrumental Neutron Activation Analysis (INAA). The radiological hazard based on Radium Equilibrium (Ra_{eq}) and External Hazard Index (H_{ex}) was assessed. In this study the activity concentration of all radionuclides in FA was enriched much higher compared to BA and FC. This work found that the degree of enrichment determined by the Enrichment Factor (EF) is differed for bottom and fly ash. The results indicated that each sample have different radiological characteristics. For Ra_{eq} and H_{ex} the values calculated for the samples were acceptable and within the limit for construction material. Generally the results proved that the values obtained were much lower and complied with the Malaysia regulatory limit and global values.

1. Introduction

Coal like any other minerals found in nature contains trace amount of such natural occurring radionuclides or Natural Occurring Radioactive Materials (NORMs). NORMs are ubiquitous in our natural environment and most of all living organisms are continuously exposed to this natural radiation from these natural radionuclides. It was reported that, the concentrations of the natural radioactive elements are similar to those in other sedimentary rocks (UNSCEAR, 2000). The naturally occurring radionuclides are Uranium and Thorium series such as ^{238}U, ^{232}Th and ^{40}K. The natural radionuclides include Uranium decay series such as ^{238}U, Uranium-234 (^{234}U), Thorium-230 (^{230}Th), Radium-226 (^{226}Ra), Radon-222 (^{222}Rn) including daughters Plumbum-210 (^{210}Pb), Polonium-210 (^{210}Po) and Thorium decay series such as ^{232}Th, Radium-228 (^{228}Ra) and Thorium-228 (^{228}Th) as well as ^{40}K (Papastefanou, 1996). These natural radionuclides may enhance their concentration due to human activities and exploitation for industrial purposes. Currently, NORM used in industries have received local and international attention due to its significant amount produced annually.

Coal is one of the major fossil fuel for electrical power generation industry and it plays an important role in energy generation sector in many countries. Coal is the most important NORM and widely available fossil fuel resources and it forms the backbone of the world’s electricity supply and will be the bedrock for many years ahead. Recently, with the uncertainty in nuclear power industry and the availability of natural gas and petroleum decreases, it has lead coal remain to be relevant (Suhana et al., 2014). Rapid urbanization and promising industrialization development program in many parts of the world have increased the usage of electricity for peaceful purposes. The demand of coal for electricity in most of developing Asian countries,

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including ASEAN is increasing and it is expected more in near future. Thus, coal potentially complementing some of renewable energy sources and will fill in the gaps in wind and solar powered electricity. Due to the benefits listed above, CFPP has become the most promising NORM industry compared to others.

NORM industries require appropriate communication strategies as to enhance public understanding on the benefits of NORM. Public needs firm answers with regards to the potential risk that they will accept from NORM industries. Thus, accurate information and trusted sources are very important for defining public's risk perception (Pineda-Solano et al., 2013). However, inadequate communication strategy can affect public's risk perception and will results to the major problems such as cancellation of existing and future expansions projects (Pineda-Solano et al., 2013).

Generally speaking, industrial coal utilization poses different environmental concerns and potential hazards throughout the whole cycle (Vairo et al., 2014). Coals burning in CFPP involve high temperature and potentially pose environmental and radiological impact. CFPP operation discharge gaseous, particulates and coal combustion by-products (CCBs) that contain radionuclides released to the atmosphere. Parallel to this, the combustion process will release CCBs and dust emission to atmosphere, generate NORM residues and wastes as well as increase in radiation background level in the environment. Detailed assessment, proper waste management and extensive research and development will reduce the CCBs generation and accumulation. In addition, these radionuclides materials are partitioned in the bottom ash, fly ash and flue gas when coal is burned (Suhana et al., 2015). These activities may contribute to environmental and radiological hazards due to the operation of CFPP and has been one of the important subject matter under study in recent years. Good collaboration among various stakeholders, such as CFPP operator and the scientist/researchers including the local community and the government are the most important criteria to solve this issue for sustainability safety development.

Coal combustion in CFPP potentially enhance the radionuclides activity concentration level (in ashes) and leads to an increase of radioactivity level in the environment due to radionuclides release and deposits on the surface soil around the CFPP area (Lu et al., 2012). Power plant operating conditions and physicochemical properties of coal have strong influenced on radioactivity level in ashes. The radioactivity level of these radionuclides may enhance by many orders of magnitudes in the ashes compared to raw coal (Suhana et al., 2015). Therefore, it is important to investigate and measure the natural radioactivity level from CFPP operation. Such measurements can then be used to assess the radiological consequences of power plant emissions (Cevik et al., 2007).

This study presents a detailed radioactivity level by an analysis of activity concentration of feed coal burned and ashes from a typical CFPP. In-depth knowledge on radiological characteristics will lead to further investigation of potential environmental and radiological hazards due to industrial application of NORM related material. If any, this warrants radiation protection towards legislative compliance in ensuring safety of the public and workers and the protection of the environment.

2. Experimental

2.1 The coal fired power plant

Table 1 presents the description of the CFPP in this study, which generated 3 x 700 MW of electricity burning sub-bituminous coal. The CFPP burns a total of 23,500 Mt of coal on a daily basis and is equipped separately with dust and gaseous emission control consisting of low NO_x burner and electrostatic precipitator (ESP) unit. It has 1 unit of stack with 150 m height. The diameter of the stack is 7.3 m.

Table 1: Description of the CFPP

Type of coal	Non-local coal, sub-bituminous
CFPP capacity (MW)	3 x 700
Total amount of coal burn per day (Mt)	23,500
Number of stack (unit)	1
Stack height (m)	150
Stack diameter (m)	7.3
Air pollution control (APC) system	Low NO_x burner and ESP

2.2 Sampling and analysis

A grab sample of FC, BA and FA was taken from the CFPP. The FC, BA and FA were collected at the coal feeder, submerged chain conveyor of the furnace and electrostatic precipitation unit. Approximately 2.0 kg of material was collected and ground to fine powder form of 200 µm in size, homogenized and air dried for about 48 h in an air circulation oven at 110 °C in the laboratory and kept in polyethylene (PE) bags. Then, approximately 500 g of each sample was sealed and kept for a period of thirty days before radioactive counting for Uranium and Thorium was performed in order to attain the radioactive equilibrium as well as to eradicate ^{222}Rn lost.

The radioactivity content of ^{238}U, ^{226}Ra, ^{232}Th and ^{40}K in the sample were measured for their activity concentration by instrumental neutron activation analysis or INAA combined with gamma spectrometry system. The Standard Reference Material (SRM) i.e. IAEA 312 for ^{226}Ra, Thorium and Uranium in soil and IAEA 313 for ^{226}Ra, Thorium and Uranium in stream sediment were used as standards in the analysis. Sample was irradiated for 300 min at open pool type 1 MW Triga-Mark research reactor of Malaysia Nuclear Agency (Nuclear Malaysia) at a thermal flux of 1.0 x 10^{12} n/cm^2.s and counted sequentially after several days by using a Gamma Spectrometry detection system. The system consist of high performance Germanium (HPGe) detector and Full Width at Half Maximum (FWHM) 1.66 keV for the 1,332 keV photo peak of Cobalt-60 (^{60}Co) and connected to a Canberra n-type multichannel analyzer. All samples were counted twice with peak areas determined by computer code GENIE 2000 software. The ^{238}U specific radioactivity content derived from the weighted mean of the activities Neptunium-239 (^{239}Np) at 228 keV and 278 keV. For ^{232}Th, specific radioactivity content derived from the weighted mean of the activities Protactinium-239 (^{233}Pa) at 312 keV. Systematic errors were taken into account for overall uncertainty calculations. The blank sample was also treated following the same procedures where the final radioactivity content in the sample was determined minus from the blank.

3. Results and discussions

3.1 Natural radioactivity in the coal and ashes

Table 2 presents the mean, standard deviation (sd) as well as the range of activity concentration in natural radionuclide ^{238}U,^{226}Ra, ^{232}Th and ^{40}K as in FC, BA and FA which showed that mean of ^{238}U in FC, BA and FA was 5.9 ± 1.1, 34.7 ± 7.1 and 47.7 ± 8.3 Becquerel per kilogram (Bq kg^{-1}). The mean activity concentration for ^{226}Ra, the daughter of ^{238}U in FC, BA and FA was 3.9 ± 1.4, 41.1 ± 5.9 and 48.4 ± 7.7 Bq kg^{-1}. Meanwhile for ^{232}Th, the mean activity concentration in FC, BA and FA was 2.7 ± 0.6, 31.3 ± 6.4 and 44.3 ± 1.5 Bq kg^{-1}. While for ^{40}K, the mean activity concentration in FC, BA and FA was 14.5 ± 4.9, 136.4 ± 26.3 and 299.0 ± 52.7 Bq kg^{-1}.

The mean activity concentrations in FC for natural radionuclide such as ^{238}U, ^{226}Ra, ^{232}Th and ^{40}K in all samples were less than the regulatory limit imposed by the International Atomic Energy Agency (IAEA) for activity concentration from radionuclide of natural origin. The regulatory limit value shall not exceed 1,000 Bq kg^{-1} for each radionuclide in the Uranium and Thorium decay series and 10,000 Bq kg^{-1} for ^{40}K (IAEA 2011).

Table 2: Measured radioactivity level of natural radionuclides in collected sample

Sample	^{238}U (Bq kg^{-1})		^{226}Ra (Bq kg^{-1})		^{232}Th (Bq kg^{-1})		^{40}K (Bq kg^{-1})	
	Mean ± sd	Range	Mean ± sd	Range	Mean ± sd	Range	Mean ± sd	Range
FC	5.9 ± 1.1	5.9 - 5.9	3.9 ± 1.4	1.2 - 9.2	2.7 ± 0.6	2.0 - 3.0	14.5 ± 4.9	9.0 - 17.9
BA	34.7 ± 7.1	25.0 - 44.0	41.1 ± 5.9	36.9 - 46.3	31.3 ± 6.4	24.0 - 36.0	136.4 ± 26.3	113.0 - 149.0
FA	47.7 ± 8.3	41.0 - 57.0	48.4 ± 7.7	44.3 - 52.2	44.3 ± 1.5	43.0 - 96.0	299.0 ± 52.7	284.0 - 309.5

Note: FC = Feed coal; BA = Bottom ash; FA = Fly Ash

As shown in Table 2, the measured activity concentrations for each radionuclide in ashes were found much to be much higher than those in FC. As expected and clearly indicates that FA has the highest activity concentration in all radionuclide compared to the other two samples. The results obtained were clearly observed that after the coal burn up, the radionuclides accumulated much higher are ashes. Higher radioactivity level may pose potential radiological hazards to the environment. The radioactivity level in ashes obtained from this study showed that the activity concentrations of ^{238}U are much higher than ^{232}Th. The radioactivity level of all radionuclides was found much higher in the finer fraction. The Clearance Limit of the activity concentration of radionuclides in residues shall not exceed 1,000 Bq kg^{-1} for both ^{238}U and ^{232}Th; and 10,000 Bq kg^{-1} for ^{226}Ra (Malaysia Radioactive Waste Regulations, 2011). Similarly, Flues et al., (2006) showed a similar pattern of high concentrations in Uranium series observed in both ashes compared to feed coal. However, the variations may occur due to the different compositions and origins of the feed coal and the use of different firing systems, furnace design and furnace temperatures (Aytekin and Baldik, 2012). In addition, these radionuclides may show different physicochemical properties resulting from different kind of behaviour and enrichment at the various stages of the combustion processes. The concentration or dispersal of radionuclides, like that of any other chemical element, is controlled by its physicochemical properties in relation to the ambient conditions (IAEA, 2003). The changes in physicochemical conditions can enrich the concentration of radionuclides, specifically in products or residues due to the industrial activities.

3.2 Enrichment Factor (EF)

An enrichment of respective radionuclides with respect to feed coal is calculated by Eq(1).

$$EF = (X)_{ash} / (X)_{coal} \quad (1)$$

Where X, is the activity concentration of an interest radionuclide divided to its activity concentration in the coal. An EF $\geq$ 1.0 means that the radionuclide is enriched in the ash compared to coal.
Table 3 present the calculated value of EFs for all samples which showed the mean value of EF for ^{238}U, ^{226}Ra, ^{232}Th and ^{40}K in bottom ash was 6 ± 1.6, 10 ± 4.1, 12 ± 3.5 and 9 ± 3.6. Meanwhile for fly ash, the mean value of EF for ^{238}U, ^{226}Ra, ^{232}Th and ^{40}K was 8 ± 2.1, 12 ± 2.6, 16 ± 3.7 and 20 ± 11.1. The activity concentration of all radionuclides in FA was enriched approximately more than eight orders of magnitudes compared to FC. The EF depends on the enrichment and volatilization behaviour of these radioactive trace elements in coal combustion. It is mostly influenced by the physicochemical properties of the specific elements, chemical compounds in coal and the CCB, the nature of combustion process and the mechanism criteria that occur at the emission control devices. EF in ashes in every radionuclide is also related to the particle size (Charro and Pena, 2013). The results shows that the sample collected at different sampling points by following their pathway in CFPP have different radiological characteristics such as natural radioactivity content and EF value.

Table 3: Calculated Enrichment Factor (EF) in coal and ashes

Sample	Enrichment Factor (EF)			
	^{238}U	^{226}Ra	^{232}Th	^{40}K
FC	-	-	-	-
BA	6 ± 1.6	10 ± 4.1	12 ± 3.5	9 ± 3.6
FA	8 ± 2.1	12 ± 2.6	16 ± 3.7	20 ± 11.1

Note: FC = Feed coal; BA = Bottom ash; FA = Fly Ash

3.3 Radium Equilibrium (Ra_{eq}) and External Hazard Index (H_{ex})

Reuse and recycle of residues related to NORM for the new product are encouraged as to reduce the accumulation of wastes as stipulated in the Malaysia Atomic Energy Licensing (Radioactive Waste Management) Regulations 2011. For an example, fly and bottom ash are widely used in cement industry for building materials or filling the underground cavities, construction of road, rail embankments and reinforced earth walls, mine filling and agriculture (Nisnevich et al., 2008).
However in this regard, the radiological hazard of the construction material based on Ra_{eq} and H_{ex} must primarily be assessed. Ra_{eq} is strongly related to external dose (gamma) and internal dose (radon and its daughters).The Ra_{eq} and H_{ex} can be calculated by the following expression as Eq(2) and Eq(3) (Beretka and Matthew, 1985).

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

$$H_{ex} = C_{Ra}/370 + C_{Th}/259 + C_K/4810 \quad (3)$$

Where, C_{Ra}, C_{Th} and C_K are the activity concentration of ^{226}Ra, ^{232}Th and ^{40}K in Bq kg^{-1}. It has been assumed that the same gamma dose rate is produced by 370 Bq kg^{-1} of ^{226}Ra or 259 Bq kg^{-1} of ^{232}Th and 4,810 Bq kg^{-1} of ^{40}K (Lu et al., 2012).
H_{ex} is determined from Ra_{eq}, by assuming that the maximum value allowed (equal to unity) as to corresponds to the upper limit of Ra_{eq}, 370 Bq kg^{-1} (Beretka and Matthew, 1985), for the safe use. It is to ensure the external dose rate will below than 1 mSv y^{-1} (ICRP, 1990). H_{ex} limit is reported as unity in order to keep the radiation hazard insignificant and the radiation exposure due to the radioactivity from construction materials is limited to 1.5 mSv y^{-1} (Beretka and Matthew, 1985).
Table 4 presents the calculated Ra_{eq} and H_{ex} value for the samples which showed the Ra_{eq} in FC, BA and FA was 9, 96 and 135 Bq kg^{-1}. Meanwhile for H_{ex}, the mean value obtained in this study was 0.02, 0.30 and 0.40.

Table 4: Calculated Radium equivalent concentration (Ra_{eq}) and External hazard indices (H_{ex}) in coal and ashes

Sample	Ra_{eq} (Bq kg^{-1})	H_{ex}
FC	9	0.02
BA	96	0.30
FA	135	0.40

Note: FC = Feed coal; BA = Bottom ash; FA = Fly Ash

As shown in Table 4, fly ash was found to record the highest Ra_{eq} and H_{ex} compared to FC and BA which concur with the enrichment factor of the activity concentration as in Table 3. This indicates the ashes are enriched in radioactivity than the feed coal. Nevertheless, the findings suggest that the calculated Ra_{eq} and H_{ex} for the samples were acceptable and safe to be reutilized.

4. Conclusions

The study on natural radioactivity in coal and ashes obtained from a coal fired power plant showed that radioactivity content level of ^{238}U, ^{226}Ra, ^{232}Th and ^{40}K in ashes were much higher that the feed coal. It was observed that the natural radionuclides activity concentration in fly ash was enriched approximately more than eight orders of magnitudes compared to the feed coal. The radioactivity levels of Uranium and Thorium in ashes mostly higher in Uranium compare to Thorium. The radioactivity content of FC, BA and FA were found less than the regulatory limit and global value in which the radiological impact of human exposure from these radionuclides is remote. In addition, Radium equilibrium concentration and External hazard indices obtained from this study were found to be acceptable and safe use for construction materials. The results presented from this typical CFPP were found to be in compliance with the regulatory limit stipulated by the law as well as the international practice. In addition, periodic monitoring of the radon gas in the workplace especially at the material handling area building which contains coal is highly recommended for future work. This is to further increase the workers' safety from unnecessary external and internal exposures when dealing with NORM.

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