NOTE

Radon exhalation from the Upper Silesian coal ashes

A. T. SOLECKI* and D. E. TCHORZ-TRZECIAKIEWICZ

Institute of Geological Sciences, University of Wrocław, pl. M. Borna 9, Wrocław 50-204, Poland

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The radon exhalation has been measured for samples of coal ashes by the can technique. In this technique, the ratio of the radon content in the air inside the can and the total radium content of the sample is often regarded to be the approximation of the emanation coefficient. In fact it is the exhalation coefficient, measure of the exhalation from the sample, and depends strongly on the sample size and geometry. Analysis of the relation between the defined exhalation coefficient and the sample thickness resulted in the exponential function. The exponential function for thickness approaching zero results in exhalation coefficient equal 13%, which can be treated as an approximation of emanation coefficient.

Keywords: radon exhalation, coal ashes, emanation coefficient, exhalation coefficient, Poland

INTRODUCTION

Emission of radioactive nuclides, which is considered as a potential risk, is mainly controlled by the local geology and structures (e.g., Durrance, 1986; Cothorn and Smith, 1987; Baixeras *et al.*, 2001; Sharma *et al.*, 2003; Yang *et al.*, 2003, 2011; Kies *et al.*, 2011; Mehra *et al.*, 2011; Tchorz-Trzeciakiewicz and Solecki, 2011; Vaupotič *et al.*, 2011; Wysocka, 2011). Risk of radon exhalation from coal ashes is a significant problem, if one takes into account the fact, that in spite of decrease in European coal mining, the lignite is still significant and prospective fuel in many countries. In the case of Poland the problem of ash storage and brown fields rehabilitation emerges due to the millions tons of production and hundreds years of potential exploitation. Uranium content of coal is, in the most cases, below 1 ppm. However, in Polish deposits, locally, uranium mineralization results in values as high as 1000 ppm (Bareja *et al.*, 1987). Therefore, uranium and thorium content and radon migrating from coal ashes are important from the ecological point of view.

Process of radon migration usually can be described by two quantities:

Radon emanation coefficient (%) describes the fraction of Rn atoms which are able to escape the solid phase of the rock (soil) and enter the air (or fluids) in the open pores. It is calculated by dividing the amount of radon released into pores by the total number of radon “born” due to radium decay in the ground (sample).

Radon flux ($\text{Bq m}^{-2} \text{s}^{-1}$) is the physical quantity describing radon release across unit surface of the ground (IAEA, 1992). Sometimes, the term **exhalation rate** ($\text{Bq m}^{-2} \text{h}^{-1}$) is used (Singh *et al.*, 1999; Tufail *et al.*, 2000; Sharma *et al.*, 2003) in the case of laboratory measurements of soil (rock) samples. Radium content and amount of radon atoms originating inside the ground (or sample) is not taken into account by evaluating radon flux.

However, if the amount of radon released from the sample is divided by total amount of radon “born” inside the sample (or total amount of decayed radium) obtained result commonly referred to as emanation coefficient (or effective radium content) should be termed as **exhalation coefficient**. In such case, not only the radium content, but the surface to volume ratio of the sample is extremely important.

Various approaches have been applied to study radon release from ground and samples. The first and most popular attempt is to measure radon concentration in soil gas, what requires either sniffing equipment or making a hole in the ground to place various radon detectors inside (Durrance, 1986; Chyi *et al.*, 2005, 2011; Yang *et al.*, 2005; Fu *et al.*, 2008, 2009; Walia *et al.*, 2008, 2009). The second way is to measure radon exhalation (flux) from the ground (or sample) by placing a cup with the detector on the ground (or sample) surface (IAEA, 1992; Al-Jarallah *et al.*, 2001; Fazal-ur-Rehmana *et al.*, 2003). The third approach is the laboratory one, where samples are put inside sealed container and radon concentration of trapped air is measured (Azam *et al.*, 1995; Jönson, 1999; Baixeras *et al.*, 2001; Oufni, 2003; Kumar *et al.*, 2005; Mahur *et al.*, 2008; Chyi *et al.*, 2010). To make the

*Corresponding author (e-mail: andrzej.solecki@ing.uni.wroc.pl)

results comparable, strict procedures with precisely defined dimensions of samples and containers are required.

In the case of the can technique the total radon content in the air (proportional to radon flux) inside the can is measured and divided by the total radium content of the sample. It is in fact the measure of the exhalation (not emanation) coefficient. It depends also on the sample thickness, since the radon atoms must leave not only minerals but the whole sample, where diffusion through coal ash layer is a dominant problem (Chauhan and Chakarvarti, 2002).

Radon release from solid bodies of various geometry is the main factor determining radon atmospheric activity over mine tailings, waste disposals and last, but not least, inside dwellings. Neither radon emanation coefficient, nor radon flux or exhalation rate can describe whole complexity of the problem. Radon emanation refers only to the internal process of the solid body, not taking into account the amount of radon released from it. In the case of radon flux or exhalation, the internal free radon content of the body is not taken into account. Thin layers of rock, soil or waste material does not attract human attention, in spite of the fact, that the majority of radon flux is generated by them and not by the huge interior of tailings, where radon is trapped inside.

In this study, the fine grained ash, remain of the Upper Silesian Carboniferous coal burning with ^{226}Ra content of 56 Bq kg^{-1} was used to study the influence of the sample thickness upon the exhalation process.

METHOD

Measurements of radium content have been performed in the landfill of coals ashes using portable Exploranium GR-320 gamma radiation spectrometer with the standard NaI (TI) GPX-21A detector of 0.35 L volume. The producer using traceable test pads performed calibration of the detector. For each measurement the detector was deployed in the field using geometry as close as possible to 2 Π . Sampling time ranged from 15 to 30 minutes depending on local radionuclides content to reach statistically significant counts. Ambient temperature during measurements was in the range 5 to 25°C.

According to producers manual impulses supplied by the detector probe were classified using channels 70–204 of the 256 channels of the spectrometer covering the energy window 850–2810 keV. Measured activities of ^{214}Bi (1760 keV peak) and ^{208}Tl (2620 keV peak) were automatically recalculated into uranium and thorium concentrations (in ppm) assuming existence of equilibrium in uranium and thorium decay series, what is a common practice in this kind of measurements marked by eU and eTh notation instead of U and Th. For further calculations the activity of ^{226}Ra was assumed to be equal to the mea-

Fig. 1. Exhalation Can arrangement in this study.

sured ^{214}Bi activity.

In the place of measurements, ash sample was taken from the area of 1 m^2 to the depth of 0.1 m. After well-mixing, representative sample of 5 kg was taken for further laboratory analysis. Radon exhalation was measured using can technique described by Azam *et al.* (1995) and modified by Solecki (1999) (Fig. 1). Eight homogenized and sieved samples of ashes with ^{226}Ra activity of 56 Bq kg^{-1} were placed in iron cans with 0.2 m high of 5 dm^3 volume, to form layers of various thicknesses (0.01, 0.026, 0.050, 0.064, 0.084, 0.103, 0.126 and 0.158 m) on the bottom of cans.

Passive open type track detectors Kodak LR115 were fixed at the top of cans and cans sealed. After 21 days iron cover held by the magnet was removed and detector exposed for 21 days in temperature of 20°C. This procedure significantly simplifies calculation procedures since radon concentration equilibrium is achieved before exposition of track detector.

After exposition detectors were etched 90 minutes in 2.5 M NaOH. Tracks were counted using optical microscope at the magnification of 100 $\times$. And then, obtained track density can be recalculated into radon concentration.

Total radon concentration in the air inside the can was divided by the total radium activity of the sample, resulting in exhalation coefficient which for very thin samples can be regarded as the approximation of the emanation coefficient. Mineral composition of the ash has been studied by XRD method. Packing density, specific density and porosity of samples were measured by water flooding method.

Fig. 2. Results of uranium (eU) and thorium (eTh) in situ measurements, mean values marked by dotted lines.

Fig. 3. Results of XRD analysis of coal ash in this study.

Table 1. Results of exhalation study

Ash layer thickness (m)	Total ^{226}Ra in ash (Bq)	Total Rn in air inside can (Bq)	Exhalation coefficient (%)
0.010	10.7	1.6	15.0
0.026	26.8	2.7	10.0
0.050	51.3	2.4	4.7
0.065	65.7	2.8	4.2
0.084	85.6	2.8	3.3
0.103	104.9	2.8	2.7
0.127	128.8	2.4	1.9
0.158	161.0	2.5	1.6

Fig. 4. Relation between layer thickness and exhalation coefficient: (A) Power trend calculated for all data; (B) Exponential trend calculated for all data; (C) Exponential trend calculated for layers thicker than 0.05 m.

RESULTS AND CONCLUSIONS

According to gamma spectrometric measurements (Fig. 2) uranium content of coal ash stored in the disposal varies in the range of 1.6 to 6.7 ppm, with mean value 4.5 ppm (56 Bq kg^{-1}). Thorium content varies in the range 3.6–17.1 ppm with mean value 12.5 ppm (51 Bq kg^{-1}).

Basic physical parameters of ash obtained in this study are: specific density, 1900 kg m^{-3} ; packing density, 740 kg m^{-3} ; porosity, 60%; activity of ^{226}Ra , 56 Bq kg^{-1} . Quartz, mullite, calcite and gypsum crystalline phases can be identified in the ash by means of XRD method (Fig. 3). Occurrence of gypsum and regenerated calcite is probably responsible for the rapid lithification of ashes observed in the field.

Results of exhalation study are presented in Table 1. Total radium content of analyzed samples varied from 10 to 160 Bq, depending on the sample size. Total amount of radon in air inside can varied from 1.6 to 2.5 Bq and exhalation coefficient varied from 1.6 to 15%.

Relation between ash layer thickness and exhalation coefficient is shown in Fig. 4, where attempts to fit various trends have been performed. The best fit for all gathered data with ($R^2 = 0.97$) has been obtained for the power trend (Fig. 4A). Good fit of obtained results to the power function $y = 3652x^{-0.8557}$ is quite reasonable taking into account the fact that surface/volume ratio of the sample is decreasing for increasing sample thickness according to formula $y = x^{-1}$. However, this kind of function reaches infinity for zero thickness value. It would require that exhalation coefficient for thinner layer approaches infinity.

Taking into account the fact, that the maximum value of exhalation coefficient cannot be higher than 100%, other trend functions available in Excel© has been applied. The best fit with highest R^2 value (0.9356) has been obtained for exponential function $y = 13.225e^{-15.056x}$ (Fig. 4B). In this case exhalation coefficient for the layer of zero thickness is 13.225%, which is quite reasonable result. For layer of 0.001 m thick, the obtained result is

13.03. Slightly better fit ($R^2 = 0.9836$) was obtained if only samples thicker than 0.05 m were taken into account (Fig. 4C). In such a case exhalation coefficient for zero thickness layer is 8.2594, and for layer of 0.001m thick is 8.17.

Considering the emanation coefficient is the fraction of Rn atoms which are able to escape the solid phase of the sample and enter air in open pores, the exhalation coefficient for layer's thickness corresponding to grain size may be regarded as approximation of the emanation coefficient. Exhalation of radon from the sample inside the can should be analyzed as three component processes: (1) emanation from mineral grains; (2) diffusion inside the ash and exhalation from the ash layer; (3) diffusion in the air inside the can. In the case of ^{222}Rn with its half life time 3.8 day, diffusion gradient for 10–20 centimeters in air of 20°C can be neglected for taking into account its air diffusion rate (Cothorn and Smith, 1987). So, the main components of the process are process-1 and -2.

The second process, diffusion inside the ash layer becomes more significant when the sample is thick. For extremely thin layer comparable with grain size only the emanation from single mineral grains exits. So, thinner the layer the more important is emanation component of the process of exhalation.

Increasing layer thickness more than 0.026 m does not significantly result in the value of exhaled radon (Table 1). The coal ash is relatively fine grained material, the radon “born” in deeper horizons of the layer cannot reach the sample surface. Obtained results indicate that measurements of exhalation for various layer thicknesses are necessary to obtain the equation which enables to estimate the emanation coefficient.

Process of radon release from fine grained coal ash material, without internal ventilation resulting from convection or atmospheric pressure, is restricted to thin external layer, no more than few centimeters thick. Such thin layers can release amount of radon comparable with huge tailings of analogous material.

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