IS COAL ASH AND SLAG ANY USEFUL OR UNLOADED WASTES?

E. Botezatu, C. Grecea, O. Iacob

Institute of Public Health, Radiation Protection Department
14, V. Babes Street, 6600 Iasi, Romania

INTRODUCTION

It is well known that all types of coal, like most materials found in nature, contain trace quantities of the naturally occurring primordial radionuclides (uranium and thorium families and potassium-40). Therefore, the combustion of coal results in partitioning of radionuclides included in the non-combustible mineral matter, between the bottom ash and fly ash, and in the release into the environment of large amounts of coal ash. Emissions from thermal power stations in gaseous and particulate form contain radioisotopes arising from the uranium and thorium series as well as from ^{40}K. They are discharged into the environment causing changes in the natural radiation background and radiation exposures to the population. The continued releases of these materials to environment may result in a buildup in the air, water and soil of the radionuclides, particularly radium-226. There will be an increase of the basic radiation rate in the neighborhood area of these plants and consequently relatively higher exposure of the local population to radiation. Coal burning is, therefore, one of the sources of technologically enhanced exposure to humans from natural radionuclides (1,2,3,4,5,6).

Coal based thermal power plants constitute about 35% of quantum of energy supply in Romania. In view of the importance of coal for energy supply in Romania, we were interested in knowing possible uses of the resulting wastes and minimize the following harmful consequences of coal burning.

METHODS

Within the framework of the study there were performed measurements of natural radioactive content in coal and wastes originating in ten representatives CFPPs and from waste piles. Extensive measurements of the levels of natural radioactivity in building materials comprising ash and/or slag and in leafy vegetables and/or grains under crop on ash/slag pile which were covered with soil were performed. The soil (top 5 cm and 5-15 cm), vegetation and food samples were collected from 400 sq. cm surface. High-resolution gamma spectrometry techniques and radiochemical and physical methods carried out in conformity with the current national standards and settlements were applied (7,8). All the solid samples were dried at 105^0C and after grinding were passed through a 12-mesh sieve. The sieved samples were placed in the plastic Marinelli beaker and stored for 30 days to allow build up and reach radioactive equilibrium of radon and its daughters. After this period those samples were measured (errors of estimation 5 %). The food and vegetation samples were dried, calcined and wet mineralized. Arising acid extracts were utilized for the assay of natural radioelements. Uranium-238 and thorium-232 were calculated after determining the content of natural uranium and thorium by the method based on their separation and purification on a strong basic anion exchange resin and spectrophotometric measurements in the form of their

Arsenazo III complex. Radium-226 was determined through its decay descendent radon-222, and by alpha rays measurement in a scintillating chamber. The assay of lead-210 was done by electrochemical deposition (65% radiochemical recovery) and beta counting of lead-210 deposited on the nickel disk using counting equipment with anticoincidence counter (20% efficiency). Potassium-40 was found by calculation after the photometry dosing in flame emission mixture of potassium natural isotopes. Measurements were performed on characteristic samples obtained from ten individual homogenized samples.

RESULTS AND DISCUSSION

The coal-fired power plants are burning brown coal, lignite and/or mixture of different kinds of coal with an ash content of 26-55 %. Large amounts of fly ash and bottom ash result from coal combustion, total ash production varying from $2\cdot10^9$Kg/Gwa up to $13\cdot10^9$Kg/Gwa. The lighter fly ash is carried to the stack, where, depending on the efficiency of the filtering system (83 – 99.5%), some fraction is collected while the rest is released to the atmosphere. The wastes are hydraulically removed to the pile, which are placed close to surface water.

- The measurements performed on coal and wastes in the coal-fired power stations clearly demonstrated the enhancement with one order of magnitude of activity concentrations over the different processing stages from coal to ash (see Table 1).

The values of activity concentrations measured in the coal samples varied over two orders of magnitude depending on the type of coal. The decreasing order of radioactivity is the following: Lignite > Brown coal > Pit coal > Pitch coal ≥ Bituminous coal.

Table 1. Mean and range activity mass concentrations in coal and wastes (Bq/kg)

Type of sample (no of samples)	Radionuclide				
	^{238}U	^{226}Ra	^{210}Pb	^{232}Th	^{40}K
Coal (114)	31 ± 2 10 – 98	45 ± 5 3 - 150	-	25 ± 16 7 - 110	300 ± 17 37 – 645
Slag and bottom ash (76)	39 ± 3 17 – 100	94 ± 5 21 - 121	149 ± 18 36 – 155	49 ± 3 15 – 129	514 ± 17 280 – 1100
Fly-ash collected (120)	144 ± 17 25 – 276	276 ± 19 140 – 460	244 ± 46 79 - 501	98 ± 23 33 – 214	547 ± 20 170 – 1265
Escaping fly-ash (34)	192 ± 56 36 – 390	380 ± 82 149 –558	260 ± 67 87 - 512	114 ± 43 41 – 360	660 ± 37 205 – 1390

The natural radionuclide concentrations in fly ash were significantly higher than the corresponding values for coal. The enrichment of natural radionuclides in fly ash increases as the size of the fly ash particles decreases (5,7,9). These smaller particles are less efficiently collected by the filtering system and thus preferentially escape from the plant, falling out in the environment. The natural radioelements from the fly ash spread in the atmosphere as sedimentable powder and fall out on the soil surface either through falling, or in association with impurities or rain. As a result of the activity deposited, we found concentrations of uranium, thorium, radium-226 and potassium-40 two times higher in the upper 5 cm layer than in the 5-15 cm layer of soils in the surrounding of the CFPPs. The highest concentrations of natural radionuclides were especially observed in the samples from the older ones. The encountered values are presented in Table 2 comparatively with usual values in Romania (10).

Table 2. Typically encountered activity concentration of natural radionuclides associated with operation of CFPPs.

Component of Environment	Location	Activity mass concentration (range)			
		^{238}U	^{226}Ra	^{232}Th	^{40}K
Soil (Bq/kg)	CFPPs	10 – 86	8 – 156	11 – 96	400 - 1200
	Usual values in Romania	8 – 60	8 – 72	11 – 75	250 - 1100
Spontaneous vegetation Bq/kg	CFPPs	0.1 – 61.0	0.7 – 40	1.5 - 83	220 - 1450
	Usual values in Romania	0.7 – 48	1.8 – 18.7	1.6 – 3.5	350 – 640

On the basis of these measurements and dose rates per unit concentration in soil, adopted from UNSCEAR (6) the average absorbed dose rate in air (at 1 m height) from gamma field of ^{238}U, ^{232}Th series and ^{40}K was estimated. The only minor excess in specific activity results in an increase in exposure to gamma rays. It was obvious that the doses were highest at locations 1-2 km from the stack as well as on the grounds of the CFPP in the direction of winds. The average value of annual absorbed dose rate in air from terrestrial gamma radiation (mGy/y) related to this non-nuclear industry (energy production using fossil fuels) is of 0.72. The value is comparable, however higher than the average value in Romania of 0.52 mGy/y (11).

- The other problem arising from CFPPs is the bulk quantity of the coal ash generated from which about 70 to 80% is disposed of in landfills or in ponds.

There are many off-site coal-ash landfills and surface impoundments, at least one per plant. A typical ash disposal landfill may be anywhere from 30 to 60 hectares. The huge amounts of solid wastes originating in coal-fired power plants CFPPs, which have technological enhanced contents of naturally occurring radioactive materials (TENORM), cover large areas of ground, giving rise to imminent ecological problems. Some of the oldest waste dumps, which have been filled, have been covered with soil and used as plough land. The potential impact of long-term accumulation of natural radioelements in the biosphere, the exposures from radionuclides that migrate through the subsoil into the environment and the use of the restored facility or land should be considered (1, 12,13).

The background radiation levels were two to fourfold higher in ash pond or dump areas, as compared to other locations in relation with operation of CFPPs. On the ash dumps the gamma dose rates ranged between 0.09 and 0.32 μGy/h. The higher levels of the radionuclide content in coal ash stored respectively in soil are reflected in the finding values for the food samples from this area. (Table 3).

Table 3. Concentrations of natural radionuclides in some food samples related to ash dump

Type of sample	Radionuclide (Bq/kg)				
	^{238}U	^{226}Ra	^{210}Pb	^{232}Th	^{40}K
Slag and ash from pile	129 ± 33 17 - 228	122 ± 29 23 - 226	-	43 ± 18 6 - 91	514 ± 17
Soil (above pile)	49 ± 17 10 - 98	109 ± 27 21 - 170	-	43 ± 12 12 - 102	560 ± 50 310 - 1145
Cereals (grains)	0.085 ± 0.021 0.036 – 0.160	0.58 ± 0.08 0.18 – 0.94	0.31 ± 0.09 0.11 – 0.53	0.115 ± 0.011 0.028 – 0.392	284 ± 27 65 – 490
Leafy vegetables	5.21 ± 0.09 0.7 - 63	8.8 ± 0.3 1 - 38	0.09 ± 0.03 0.04 – 0.25	9.7 ± 1.4 2.2 - 74	478 ± 31 230 - 910

One can see the high variability of values of natural radioelemnts concentrations especially in the foodstuffs. The values of measured concentrations in harvest on oldest piles are comparable but higher than the corresponding values for the same cereals in Romania, especially for uranium and radium (6, 10, 14,15).

- Roughly a third of coal ash is re-used mainly as substitutes or as an additive in cement and concrete, as structural fills for buildings and road construction, in land reclamation, in roofing materials and various products used as building materials (1, 2, 4, 16, 17).

We have investigated the conventional and non-conventional building materials used in dwelling construction. The conventional building materials - currently in use in Romania- have mean activity mass concentrations of 51±32 Bq/Kg ^{226}Ra, 48±34 Bq/Kg ^{232}Th and 532±158 Bq/Kg ^{40}K, which are considered as reference levels. Non-conventional building materials which contain industrial wastes and by-products have 370±200 Bq/Kg of ^{40}K and higher concentrations of ^{226}Ra (120±70 Bq/Kg) and ^{232}Th (100±59 Bq/Kg) (18, 20, 21). We have selected some building materials (cement, concrete, coal cinder and clinker bricks, prefabricated blocks and boards, autoclaved cellular concrete), that have widely incorporated into them fly ash or slag from CFPPs as a constituent. The mean concentration of the natural radionuclides ^{226}Ra, ^{232}Th and ^{40}K in these materials has values of 95±16 Bq/Kg, of 65±12 Bq/Kg and of 404±81 Bq/Kg, respectively. One can see that although the CFPP's wastes contain much higher concentrations of natural radioelements, their use in combination with other materials produced concentrations approaching values for conventional materials excepting radium-226 level that is nearly twice higher (Table 4).

Table 4. Mean specific activity determined in selected building materials and classification of these building materials.

Type of material	Mean specific activity (Bq/kg)			Activity index/Category
	^{226}Ra	^{232}Th	^{40}K	
Wastes used in building materials				
Slag	104 ± 52	64 ± 37	564 ± 300	0.854 / II 0.4 – 1.3/ I-III
Coal fly ash	288 ± 164	130 ±109	665 ± 400	1.83 / II 0.6 – 3/ II-III
Most common building materials containing wastes				
Cement PA (21)	74 ± 59	27 ± 8	281 ± 148	0.44 / I 0.2 – 0.8/ I-II
Concrete (ballast , pumice, foamed, aerated and light weight, heavy) (43)	69 ± 51	77 ± 69	918 ± 519	0.92 / II 0.2 – 1.6/ I-III
Clinker bricks (23)	52 ± 4	56 ± 26	531 ± 115	0.63 / II 0.4 – 0.8/ I-II
Granulates (19)	53 ± 43	40 ± 13	447 ± 143	0.52 / II 0.3 – 0.8/ I-II
Coal-cinder bricks (11)	139 ± 84	57 ± 32	196 ± 153	0.81 / II 0.3 – 1.3/ I-III
Prefabricated coal shovel blocks (14)	124 ± 95	48 ± 18	291 ±149	0.75 / II 0.3 – 1.2/ I-III
Autoclaved cellular concrete, white (32)	114 ± 79	115 ± 58	357 ± 309	1.07 / III 0.4 – 1.7/ I-III
Autoclaved cellular concrete, gray (35)	95 ± 26	90 ± 93	485 ± 650	0.928 / II 0.2 – 1.7/ I-III

(n) Number of samples analysed

Utilisation of fly ash and other coal combustion by-products in concrete, in everyday construction applications and other civil engineering applications has important technical and economic advantages because these are abundantly available materials. Their use in the building materials industry could partially serve to help clear up ecological problems arising from disposed ash, but may also increase the potential for the occurrence of unpredictable exposures (10, 18, 19). Sometimes, we met the poor situations in some P+4 blocks of flats, where the coal ash and slag were used just as cement substitutes (ranging from 0.4 to 4.9 %) and therefore the doses were higher (21).The use of coal ash as a building material is subject to strict control by the National Radiation Hygiene Laboratory Network of the Health Ministry in Romania. There is concern that fly ash may become regulated in the future, which would discourage reuse.

The radiological consequences (potential high indoor radiation doses) of using these types of materials in the dwelling construction have to be discussed related to further individual and collective risks. With a view to knowing the radiological significance of these values, we calculated an activity concentration index (I) in accordance with radiological protection principles concerning the natural radioactivity of building materials (22).

$$I = (C_{Ra}/300\ \mathrm{Bq\ kg^{-1}}) + (C_{Th}/200\ \mathrm{Bq\ kg^{-1}}) + (C_{K}/3000\ \mathrm{Bq\ kg^{-1}})$$

Where C_{Ra}, C_{Th}, C_{K} are the radium, thorium and potassium activity concentrations (Bq kg^{-1}) in the building materials.

By applying this activity concentration index, we succeeded in defining 3 categories of building materials, in accordance with the average content of natural radioelements determined in these materials, typical ways and amounts in which the material is used in a building. The classification of the selected building materials was performed using this index (I) which is derived for identifying whether a dose criterion is met. The activity concentration index shall not exceed the values of 0.5 respectively 1, depending on the dose criterion of 0.3 mSv a^{-1} (*Category I*), respectively 1 mSv a^{-1} (*Category II*) which is required. Building materials containing the highest levels of natural radioactive content belong to the *Category III* (see Table 4).

According to this classification, the building materials that have in their composition fly ash or bottom ash belong to the building materials with medium radioactive levels and can be used in the building industry. One can accept the unrestricted use of building materials having a less than one index for activity concentration. When this index is greater than one, it is necessary to calculate the mean weighted of natural radioactive elements concentrations over the whole building. If the outcome index of gamma radiation is less than one, the reference will be favorable for using it as building material. Within the European Union, doses exceeding 1 mSv a^{-1} should be taken into account from the radiation protection point of view (22).

Because the separate limitations for radon and thoron exhaling from building materials should be considered, (4, 6, 22) we calculated the average flux density of radon for a representative wall entirely built from each material selected (Table 5). The highest values were obtained for autoclaved cellular concrete.

Table 5. The flux density (I_D) for ^{222}Rn and ^{220}Rn for a representative wall

Building material	I_D ^{222}Rn (mBq/ m^2 s)	I_D ^{220}Rn (mBq/ m^2 s)
Cement PA	1.4 ± 0.3	120 ± 45
Concrete (ballast , pumice, foamed, aerated and light weight, heavy)	3.1 ± 1.1	355 ± 170
Clinker bricks	2.1 ± 0.3	260 ± 130
Granulates	2.2 ± 1.8	180 ± 60
Coal-cinder bricks	5.9 ± 3.5	260 ± 145
Prefabricated blocks	5.2 ± 3.9	220 ± 80
Cinders concrete	4.3 ± 2.9	420 ± 190
Autoclaved cellular concrete, white	4.8 ± 2.2	530 ± 260
Autoclaved cellular concrete, gray	3.9 ± 1.1	410 ±250

CONCLUDING REMARKS

- The Coal Fired Power Plants are a potential radioactive polluting source for the environment due to the atmospheric discharges of escaping fly ash as well as to the presence of ash dumps. Coal consumption generates large amounts of coal ash that require proper management and disposal, either at the point of use or elsewhere in ash stored facilities.
- The retained ash is enriched in uranium, radium and thorium several times over the original activity concentrations in the coal.
- The question of recycling wastes originated in CFPPs in building materials and their use in building industry must be posed in terms of finding an optimal solution that would enable their use to a higher extent, while accepting a minimum health risk. A prudent attitude must be adopted versus certain ashes with a highest natural radioactive content for the use in mixture with other materials for dwelling construction.
- Among the undoubtful advantages that such unconventional building materials may offer there could be mentioned:

- the preservation of natural resources,
- the decrease in the production cost,
- the clearing of some surfaces which might be given back to economic circulation
- the ecological advantages connected with environment pollution control.

- The disadvantages are of a radiological origin, respectively, the possible higher internal and external radiation doses for inhabitants.

REFERENCES

1. Eisenbud M., Gesell T., (1997), *Environmental Radioactivity from Natural, Industrial and Military Sources*, Inc. 4th ed., Ch. 6, Academic Press, Morgan Kaufmann Publishers, Idaho.
2. Kraus W., Kendall G. M., (1999), *Examples of enhanced exposure to natural radiation,* Proc. 6thInt. Symp. on Achievements & Challenges: Advancing Radiation Protection into the 21st Century, Southport, UK, 69.
3. Martin A., Mead S., Wade B. O., (1997), *Materials Containing Natural Radionuclides in Enhanced Concentrations*, European Commission Report EUR 17625.
4. Smith K.R., Crockett G. M., Oatway W. B., Harvey M. P.,(2001), *Radiological Impact on the UK Population of Industries which Use or Produce Materials Containing Enhanced Levels of Naturally Occurring Radionuclides: Part I, Coal Fired Electricity Generation*, NRPB Report 327, Didcot, Oxon.
5. UNSCEAR, (1993), *Exposure from Natural Sources of Radiation*. Report Annex A, UN, New York.
6. UNSCEAR, (2000), *Exposures from Natural Radiation Sources,* Report Annex B, UN, New York.
7. Botezatu E., Gradinaru M., Grecea C., (1993), *Coal Fired Power Plants as Source of Population Exposure,* J. Prev. Med., **1,** 1, 15-20.
8. Botezatu E., Aflorei A., (1997), *Non-nuclear industries involving natural radioactivity impact on the environment and workplaces,* J. Prev. Med., **5**, 4, 13-21.
9. Ramachandran T.V., Mishra U.C., (2000), *Technologically Enhanced Natural Radiation Due to Coal Fired Power Plants in India,* Proc. 5thInt. Conf. on HLNRRA: Radiation Dose and Health Effects, Munich, vol. 2, 321.
10. Romanian Society for Radiological Protection (RSRP), (1994), *Natural radioactivity in Romania*, Bucuresti.
11. Iacob O., Botezatu E., Grecea C., (2000), *Update on Natural Radiation Exposures in Romania*, Proc. 5thInt. Conf. on HLNRRA: Radiation Dose and Health Effects, Munich, vol. 2, 7.
12. Botezatu E., Grecea C., Botezatu G., (1996), *Radiation Exposure Potential from Coal-Fired Power Plants in Romania*, Proc. 9th Int. Congress on Radiation Protection, Vienna, vol. 2, 196.
13. Kljajic R., Masic Z., Mitrovic R. M., (1996), *Radiation Exposure of the Population in the Vicinity of Coal-Fired Power Plants*, Proc. 9th Int. Congress on Radiation Protection, Vienna, vol. 2, 223.
14. Botezatu E., (1996), *The Natural Radioactivity of some foodstuff from Moldova,* Proc. 9th Int. Congress on Radiation Protection, Vienna, vol. 2, 202.
15. Botezatu E., (1994)*, Contribution of the Dietary Ingestion to the Natural Radiation exposure of Romanian Population,* J. Hyg. Public Health, **44**, 1-2, 19-21.
16. Koperski J.G., (2000), *Misapplication of the IAEA 1996 Basic Safety Standards to the Minerals Industry – Impact on the NORM and TENORM Issues,* Proc. 10th Int. Congress IRPA on Harmonization of Radiation, Human Life and the Ecosystem, Hiroshima.
17. Menon S., (1999), *The Regulation of NORM from a Nuclear Decommissioner's Viewpoint*, WM'99 Conference, February 28 – March 1.

18. Botezatu E., Iacob O., Grecea C., Miron C., Clain L, Grãdinaru M., (1999), *Radiological consequences of industrial wastes used as building materials,* J. Prev. Med., **7**, 3, 20-30.
19. Nemeth C., Somlai J., Nenyei A., Skrinyar M., (2000), *Dose in Buildings Caused by Built-in Coal-Slags with Elevated ^{226}Ra Concentrations and the Possibilities of Intervention*, Proc. 10th Int. Congress IRPA on Harmonization of Radiation, Human Life and the Ecosystem, Hiroshima, vol. 1, 27.
20. Grãdinaru M., Clain L., Botezatu E., (1995), *The natural radioactivity of building materials,* J. Prev. Med., **3**, 3-4, 9-15.
21. Botezatu E., Clain L., Iacob O., (2000), *Increased Indoor Radiation Exposures – Consequences of NORMs in Building Materials*, Proc. 5thInt. Conf. on HLNRRA: Radiation Dose and Health Effects, Munich, vol. 2, 355.
22. EUROPEAN COMMISSION, (1999), *Radiological Protection Principles Concerning the Natural Radioactivity of Building Materials,* Radiation Protection 112.