Main Characteristics of the Radioactive Enrichment in Ashes Produced in Coal-Fired Power Stations

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Abstract. Under contract with the Spain's "Nuclear Safety Council", a study is being conducted of the nation's largest nominal output coal-fired power stations. Its purpose is to assess the radiological impact on workers and local populations due to this source of NORM activity. One of the aspects of particular interest is the study of the radioactive enrichment in the combustion wastes relative to the different coals used as fuel (usually local bituminous coal or lignite, or imported coal). These wastes consist of fly ash (mostly fine particles collected in electrostatic precipitators), and bottom ash (larger in size, and collected wet or dry in hoppers below the boilers). In general terms, the enrichment factors measured were between 2 and 18 for the radionuclides ^{40}K, ^{226}Ra, ^{232}Th, and ^{210}Po. The magnitude of this enrichment factor depended mainly on the ash content of each coal, and hence on the type of coal used as fuel and the specific operation cycle in the different power stations. For the radionuclides ^{40}K, ^{226}Ra, and ^{232}Th, the enrichment was relatively similar in value in the fly and bottom ashes produced by the different types of coal used in the power stations studied. For ^{210}Po, however, as was expected, the enrichment was much greater in the fly ash than in the bottom ash for each coal analyzed.

KEYWORDS: NORM, Coal-fired power stations, symmetric or asymmetric enrichment, coals, ashes

1. Introduction

Currently, a research group consisting of members of the Radiological Protection of the Public and Environmental Unit, CIEMAT, and the Environmental Radioactivity Laboratory at the University of Extremadura, funded by the Nuclear Safety Council, is conducting a Research Project entitled "Study of the Radiological Impact of Coal-Fired Power Plants on their Surroundings".

The scope of that project was limited to the four largest nominal output coal-fired power stations (CFPPs) in Spain – As Pontes (CFPP-1), Carboneras (CFPP-2), Compostilla (CFPP-3), and Teruel (CFPP-4). Their approximate locations are shown in Figure 1. These plants were chosen because they present a series of interesting circumstances: first, their size, and hence the large amount of coal they use and ash they produce; second, their locations, since these correspond to very different climatic characteristics which may influence the dynamics of any radionuclides evacuated; third, the very different origins and characteristics of the coal the four plants use, which in principle should have different radioactive contents; and fourth, the different dates at which they became operational, which could at least in part influence their mode of operation, and the generation and treatment of their waste.

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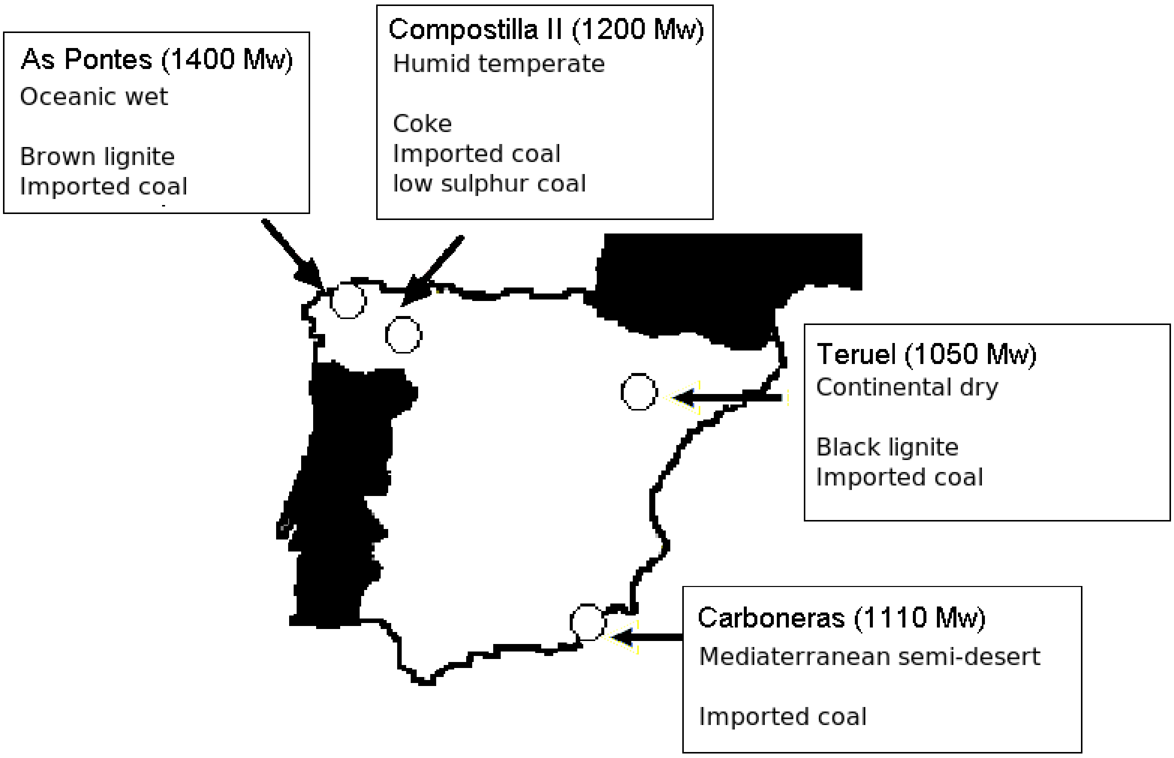
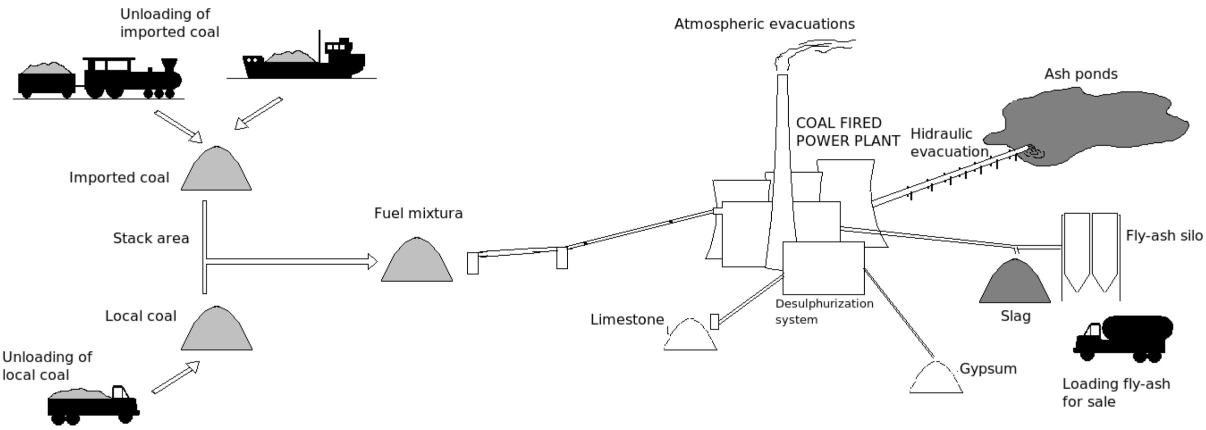
Figure 1: Location of the conventional thermal power stations studied, their nominal power, the prevailing climate in the area, and fuel customarily used.



To produce 1 GW of electricity in a CFPP, it is necessary to burn about $3 \cdot 10^9$ kg of coal [1]. These plants thus consume enormous amounts of fuel in relatively short periods of time. They therefore have specially prepared zones for the accumulation of vast amounts of coal in storage piles. The coal reaches these zones by very different means of transport, as is shown in Figure 2. Its origin can vary according to conditions in the international coal market, and to the capacity of the plant's boilers to burn different types of fossil fuels. The mix for consumption is prepared from these storage piles by means of specialized machinery and with the aid of mechanical shovels.

This mix is normally loaded into hoppers with mechanical shovels, from which it is transported by conveyor belt to pulverizing mills. The resulting powder is sprayed by a stream of preheated air through the burners into the boiler. The temperature of combustion depends on the design of each boiler, but can be up to about 1700°C. In the combustion process, most of the coal's mineral content melts, forming a vitrified ash. The heavier part of this ash, together with incompletely burnt organic matter, falls to the bottom of the boiler in the form of a coarse bottom ash or clinker, which is removed either wet or dry, and deposited in specifically prepared zones, such as artificial ponds, slag heaps, or mines. To reduce, at least in part, the accumulation of this type of waste, it is usually recycled as part of various construction materials. The lighter part of the ash, the fly ash, together with the hot combustion gases and volatile mineral compounds, pass through the boiler to the electrostatic precipitators. These retain practically all the fly ash, with retention efficiencies greater than 99.5% in modern CFPPs, by applying potential differences of the order of 70 kV. In some plants, the fly ash is deposited onto rafts equipped for that purpose, but now it is usually stored in silos for subsequent sale. Finally, the combustion gases are evacuated directly into the atmosphere, although in those plants where the fuels used have high sulphur contents, such as CFPP-4, prior to their evacuation the combustion gases pass through a desulphurization system, in which a supply of water and limestone yields gypsum as a byproduct, leaving the flue gases very efficiently desulphurized.

Figure 2: Diagram of operation of a typical coal-fired power plant (CFPP).



2. Materials and Methods

For the measurements of the samples of interest in the present study, we used a high resolution, low background, gamma spectrometer consisting of a coaxial p-type intrinsic germanium detector with a 45% relative efficiency, 1.9 keV resolving power, and 56:1 peak-to-Compton ratio for the ^{60}Co 1332.5 keV emission. This detector is housed in low-activity lead shielding, with an interior lining of copper to attenuate the X-rays from the shielding itself. The spectra are stored in a DSPEC 4096-channel multichannel analyzer. The detector efficiency was calibrated using certified mixed gamma standards QCY-48 (energy range 60–1900 keV) supplied by Amersham. The accuracy of the measured levels was validated against systematic measurements of two IAEA reference soils, identified as Soil 6 and Soil 327. Prior to their gamma spectrometric assay, the samples were put into 191 cm3 volume Petri dishes, covered, and sealed to prevent ^{222}Rn losses. Measurements were made no sooner than 28 days after sealing to ensure secular equilibrium between ^{222}Rn and its descendants. The systematically analyzed photopeaks were: ^{214}Pb (351.9 keV), ^{208}Tl (583.1 keV), ^{214}Bi (609.3 keV), ^{228}Ac (911.1 keV), and ^{40}K (1460.7 keV). The activity of ^{226}Ra was determined from the mean of the activities of ^{214}Pb and ^{214}Bi in secular equilibrium, and similarly that of ^{232}Th from the activities of ^{208}Tl and ^{228}Ac.

The ^{210}Po activity was determined by alpha spectrometry. To this end, a prior radiochemical separation of Po was performed as follows. First, the matrix was subjected to acid digestion, followed by the addition of a tracer, ^{208}Po. The resulting solution was then preconcentrated by forming a precipitate of $Fe(OH)_3$ on which the polonium present in the sample is adsorbed. The sample was finally conditioned in acidic medium with 1.5 M HCl, including the addition of ascorbic acid to avoid interference of the Fe content and facilitate autodeposition onto a silver planchet previously impermeabilized on one side.

3. Results

3.1. Activity measurements of samples of different types of coal

Samples were taken of the different types of coal used in the four conventional thermal power plants studied. The boilers of each plant are specifically designed to burn one or more types of coal with certain characteristics. Due to demand forces in the coal market and the regulations governing emissions of sulfur and nitrogen compounds through the chimneys, some of these plants currently use a mix of different types of coal in specific proportions as fuel. First, we determined that activity levels of the different coals purchased by the four power plants. Table 1 presents the results.

Table 1: Levels and ranges of the average activity measured in the analysis of the different types of coal used by the four CFPPs.

Coal	Coal fired Power Plant	Activity (Bq/kg)		
		^{40}K	^{226}Ra	^{232}Th
Imported coal	CFPP-1	< 10	3 ± 2	3 ± 3
	CFPP-2	62 ± 29	18 ± 4	19 ± 5
	CFPP-3	47 ± 12	30 ± 2	30 ± 3
	CFPP-4	< 83	29 ± 6	23 ± 5
Low sulphur coal	CFPP-3	462 ± 15	35 ± 3	36 ± 4
Petroleum Coke	CFPP-3	< 20	4 ± 2	< 6
Brown lignite	CFPP-1	82 ± 16	12 ± 3	10 ± 4
Black lignite	CFPP-4	113 ± 32	63 ± 6	19 ± 5
UNSCEAR [2]	V_m	400	35	30
	Range	140 - 850	17 - 60	11 - 64

In view of these results, one can state that in general the coals used by the four largest CFPPs in Spain present levels of activity of ^{40}K, ^{226}Ra, and ^{232}Th within the ranges given in the UNSCEAR report [2]. Nonetheless, there stand out the low concentrations of these radionuclides in the imported coal used by CFPP-1 and the petroleum coke, although the latter result was expected since this product is derived from petroleum in which the concentration of these radionuclides is significantly lower than in coal [2],[3]. Moreover, it should be noted that these four largest Spanish CFPPs use imported coal as fuel, either exclusively or mixed in different proportions with other coals. One observes that not all the samples of imported coal collected have similar levels of activity, suggesting that their origins are different. Another fact worth noting is the difference in the ^{226}Ra activity levels of the lignite ("brown coal") and sub-bituminous coal ("black lignite") samples. Indeed, the ^{226}Ra activity concentrations detected in the latter slightly exceed the range of activities for this radionuclide given in the UNSCEAR report [2].

3.2. Activity measurements of samples of fuel, fly ash, and bottom ash: Enrichment factors

As was indicated above, samples of the different fuels used by the four CFPPs were collected, either of the pure coals or of the mixtures currently being used as fuel. We also collected samples of the fly and bottom ashes generated by the combustion of these fuels. The results of the activity measurements of these two groups of samples are presented in Table 2. In the table, one appreciates the different mixes of fuel used in each plant and the corresponding different levels of activity. No values were detected that differed significantly with respect to those cited in the UNSCEAR report as global averages. However, there were significant differences in the ^{40}K, ^{226}Ra, ^{232}Th, and ^{210}Po activity levels of the fly and bottom ashes between the different plants, even when the activity levels of the fuel they were using were similar. The probable reason for this finding is, on the one hand, the different boiler designs, and, on the other, the different mineral content of the fuels. Indeed, the combustion of the fuels with a higher mineral content as a general rule produced fly and bottom ashes with lower concentrations of radionuclides.

Table 2: Activity levels measured in the fuels, fly ash, and bottom ash collected at each plant. Nm: Not measured.

Coal Fired Power Plant		Activity (Bq/kg)			
		^{40}K	^{226}Ra	^{232}Th	^{210}Po
CFPP-1	Fuel (Lignite, Coal)	82 ± 16	12 ± 3	10 ± 4	Nm
	Fly-ash	263 ± 13	50 ± 3	47 ± 3	Nm
	Slag	114 ± 25	19 ± 4	19 ± 6	Nm
CFPP-2	Fuel (Coal)	62 ± 29	18 ± 4	19 ± 5	47 ± 20
	Fly-ash	249 ± 145	156 ± 48	154 ± 53	962 ± 154
	Slag	224 ± 145	144 ± 55	138 ± 61	9 ± 4
CFPP-3	Fuel (Coke, Coal, Low S coal)	325 ± 17	34 ± 3	35 ± 4	91 ± 12
	Fly-ash	1160 ± 22	100 ± 5	97 ± 5	350 ± 60
	Slag	1100 ± 20	86 ± 3	90 ± 5	15 ± 8
CFPP-4	Fuel (Black Lignite /Hulla)	77 ± 29	56 ± 6	21 ± 5	65 ± 11
	Fly-ash	310 ± 25	190 ± 16	75 ± 5	257 ± 30
	Slag	240 ± 20	150 ± 10	66 ± 5	57 ± 7

The ^{40}K, ^{226}Ra, ^{232}Th, and ^{210}Po enrichment factors were calculated for the fly and bottom ashes from the activity levels listed in Table 2. The results are presented in Table 3. Firstly, one notes that these values are coherent with those frequently reported in the literature, as reflected in the ranges given in this last table. In particular, Bem et al. [6] report enrichment factors for the radionuclides studied here of about 3.5 between coal and bottom ash, and of about 5 between coal and fly ash. Secondly, there has to be noted the different enrichment factors of the radionuclides studied between the bottom ashes and the fly ashes. This difference may be associated with the combustion in the boiler, the partition of the radionuclides between the bottom ash and the fly ash, etc. [4]. This effect was particularly marked for ^{210}Po, since its activity concentration was less in the bottom ash than in the corresponding fuel. Since Po is a volatile element at the temperature of combustion of the boiler, it is very likely to have been concentrated in the fine particles of the fly ash relative to the bottom ash [5].

Table 3: Enrichment factors of the ^{40}K, ^{226}Ra, ^{232}Th, and ^{210}Po activity levels in the fly ash and bottom ash relative to the corresponding fuel burned.

Coal Fired Power Plant		Enrichment factor			
		^{40}K	^{226}Ra	^{232}Th	^{210}Po
CFPP-1	Fuel - Fly-ash	3,2	4,2	4,7	Nm
	Fuel - Slag	1,4	1,6	2	Nm
CFPP-2	Fuel - Fly-ash	4	8,7	8,1	18
	Fuel - Slag	3,6	8	7,3	0,17
CFPP-3	Fuel - Fly-ash	3,4	2,6	2,6	5,4
	Fuel - Slag	3,4	2,6	2,6	0,16
CFPP-4	Fuel - Fly-ash	4,3	3,4	3,5	4,0
	Fuel - Slag	3,3	2,7	3,2	0,88
Fly-ash range [1]		10-50	5-15	1-10	30-200

4. Conclusions

The activity levels of ^{40}K, ^{226}Ra, ^{232}Th, and ^{210}Po in the fuels used in Spain's four largest coal-fired power plants, whether consisting of a single type of coal or a mixture of different types, were within the range of values given in the UNSCEAR report [2]. The enrichment in the concentrations of these radionuclides in the bottom and fly ashes produced in these plants not only depended on the type of fuel used, but also on the specific characteristics of each plant's combustion process. This enrichment was consistently greater in the fly ash than in the bottom ash except for the case of ^{210}Po, for which, due to the volatility of this element during the combustion of the coal in the boilers, there was no enrichment.

5. Acknowledgements

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6. References

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