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Behaviour of natural radionuclides in coal combustion

J.C. Mora[1], A. Baeza[2], B. Robles[1], J.A. Corbacho[2] and D. Cancio[1]

[1]*Unit of Radiological Protection of the Public and Environment, CIEMAT,*
Avda. de la Complutense 22, 28040 Madrid, Spain
[2]*Environmental Radioactivity Laboratory, University of Extremadura,*
Avda. de la Universidad SN, 10071 Cáceres, Spain

Abstract. The study presented here, being its main goal to evaluate the behaviour of natural radionuclides in coal combustion, is part of a wider study carried out by CIEMAT and the University of Extremadura (UEX). The research is addressed to the radiological evaluation of the workers and the public as a result of the operation of the four biggest Spanish Coal-Fired Power Plants (CFPPs). Some generally used effects were confirmed in this study, as the difference in concentration of ^{210}Po in fly and bottom-ashes. Enrichment factors relative to ^{40}K as defined by UNSCEAR were found to be a little different than expected. ^{210}Po enrichment was found in gypsum (material obtained as a by-product in the desulphuration process). In order to confirm the assumption considered to explain difference in ^{232}Th activity concentration between bottom and fly ashes, carbon content was measured, obtaining that it should be reviewed.

1. INTRODUCTION

Natural radioactivity is ubiquitous in every material on earth crust; therefore it is present in coal. The variability of the specific activity depends mainly on chemical and physical conditions in which materials were formed. In coals, natural radioactivity is usually lower than in other minerals. However, some radionuclides can be found in important specific activities under special conditions, as in uraniferous coals [1]. Human modifications on coal for its use involve increments in radioactivity that cause to consider it a NORM industry [2]. This industry is usually divided in mining and combustion, the last mainly for electricity generation. In this work only modifications after mining were investigated.

2. DISCUSSION

A first modification to be considered is the loss of part of the radon gas that is present inside the coals, in the processes of mining and milling. However usually all radon isotopes are supposed to be emitted to the atmosphere by the stacks, considered in secular equilibrium with their parents.

In the combustion process some effects should be considered, being the main one the concentration of every radioactive material due to the elimination of carbon, water and radon, that amount about a 70% of the initial mass in coal (depending on the type). Every chemical element with boiling point above the temperature reached in the boilers will remain in solid state, forming part of the ashes. Temperatures considered in this work range from 1700 °C inside the boiler to 80 °C for the discharged gases. This main concentration effect can be quantified as $k = \alpha^{-1}$, being α the solid residue content in coals and k the 'main enrichment factor'.

Using the limit specifications of the studied Spanish coal-fired power plants (CFPPs) a main enrichment factor (k) from 5 to 20 can be calculated to be possible. Instead, depending on the coal that is being used, the solid residue content α can range from 11% to 30% and so, sometimes, different coals must be mixed to reach the limit specifications [3].

In the studied CFPPs, which operate every year for more than 70% of the time, and with a power above 1 GW, around $5 \cdot 10^6$ Tons of coal are used annually, generating from $5 \cdot 10^5$ to 10^6 Tons of ashes where radioactivity is concentrated. In potassium and thorium, which present higher boiling points, the aforementioned main enrichment factor k (5–20) should be obtained. In the studied CFPPs, k values ranging from 3 to 9 were found.

Other effects that affect the specific activities should be considered for the different radionuclides in the waste flows. An effect which was described being that not burned material accumulate in bottom ashes [1], causing therefore lower specific activities than in fly ashes.

Those elements with boiling point below the temperature that is reached inside the boilers evaporate and recombine with other elements in the flue gases, forming different chemical species. If the boiling point of these new generated compounds are lower than the final gas temperature (80 °C), they will condensate before their discharge to the atmosphere. This condensation might occur in particles suspended in the flue gases (fly ashes), or in the coldest points of the structure, as can the heat exchange systems be [4]. This mechanism forms an external layer, soluble in water and enriched in lead, around the fly ashes. This is the cause of the concentration of ^{210}Pb and its daughter ^{210}Po in fly ashes, which increase as particle size decrease. This behaviour can be modelled using some reasonable assumptions.

Due to environmental regulations, sequential filtering systems are usually applied to the flue gases. Those systems can be mechanical, chemical or electrostatic. They present additional concentration effects in flue gases and in the suspended particles. Scrubbers and electrostatic precipitators take away the gross particles that are recollected and usually dropped into ponds or reused as part of construction materials.

Other systems used are desulphuration plants, using wet or dry systems, in which flue gases react with a cheap material as limestone ($CaCO_3$), giving rise to gypsum ($CaSO_4 \cdot 2H_2O$). When wet systems are used, the external layer of the fly ashes could be dissolved in water, thereby increasing the gypsum concentration.

All these effects must be studied in order to carry out systematic evaluations.

3. MEASUREMENTS AND CALCULATIONS

Measurements on every material used and the waste generated in two Spanish CFPPs with different characteristics (UPT Teruel and UPT Litoral groups 1 and 2), were carried out. The systems used to measure specific activities were mainly gamma and alpha spectrometry. The results obtained for the different raw materials used in both plants, presented as weighted means, are presented in Table 1, while results for wastes are in Table 2.

Table 1. Results for raw materials measured in UPT Teruel (T) and UPT Litoral (L1 = group1 and L2 = group2).

	Lignite (T)	**Bituminous coal (T)**	**Mix (70%–20%) (T)**	**Limestone (T)**	**Bituminous coal (L1)**	**Bituminous coal (L2)**
^{40}K	104 ± 15	<20	66 ± 15	35 ± 12	70 ± 16	45 ± 15
^{226}Ra	64 ± 3	30 ± 3	54 ± 3	20.0 ± 1.4	15 ± 3	19.3 ± 2.4
^{232}Th	18 ± 3	25 ± 3	21 ± 3	<5	13 ± 3	20 ± 3
^{210}Po	-	-	65 ± 11	<0.8	33 ± 4	61 ± 6

Table 2. Results for wastes measured in UPT Teruel (T) and UPT Litoral (L1 and L2).

	Fly ash (T)	**Bottom ash (T)**	**Gypsum (T)**	**Fly ash (L1)**	**Bottom ash (L1)**	**Fly ash (L2)**	**Bottom ash (L2)**
^{40}K	306 ± 13	235 ± 11	20 ± 17	338 ± 16	278 ± 16	164 ± 15	161 ± 12
^{226}Ra	191 ± 9	149 ± 6	15.3 ± 1.7	107 ± 4	81 ± 4	173 ± 7	162 ± 6
^{232}Th	74 ± 3	66 ± 3	<5	87 ± 4	64 ± 4	173 ± 6	153 ± 5
^{210}Po	257 ± 30	57 ± 7	27 ± 3	300 ± 40	7 ± 1	386 ± 40	7 ± 1

The average main enrichment factor (k) for ^{40}K in Teruel is calculated to be 4.6 for fly ashes and 3.6 for bottom ashes while in Litoral is 6.1 and 5.4 for fly ashes and bottom ashes respectively. Using an averaged fly and bottom ashes k factor, a solid residue content (α) in coals of 24% in Teruel and 17% in Litoral is obtained, in good agreement with the data provided by the plants.

Using a relative enrichment factor (EF) for other radionuclides in the residues [1], relative to the ^{40}K (1) the results presented in Table 3 are obtained.

$$EF = \frac{[X]_{\text{sample}} / \left[{}^{40}\text{K}\right]_{\text{sample}}}{[X]_{\text{coal}} / \left[{}^{40}\text{K}\right]_{\text{coal}}} \tag{1}$$

Table 3. EF relative to ^{40}K measured in the CFPPs ashes.

	Teruel			**Litoral 1**			**Litoral 2**		
	^{226}Ra	^{232}Th	^{210}Po	^{226}Ra	^{232}Th	^{210}Po	^{226}Ra	^{232}Th	^{210}Po
Fly ash/coal	0.8	1.3	1.3	1.5	1.4	1.9	2.5	2.4	1.8
B. ash/coal	0.8	1.1	1.1	1.4	1.2	0.05	2.4	2.2	0.03

For the gypsum an absolute decrease in ^{40}K (43%) and ^{226}Ra (24%) can be observed respect to the limestone, while for ^{232}Th the detection limit does not allow to quantify any change. For ^{210}Po an absolute enrichment compared with limestone greater than a factor 36 was measured in this material.

In order to verify if not burned material is accumulated more in bottom ashes than in fly ashes, elemental carbon content in ashes was measured. Results for the measured samples can be found in Table 4.

Table 4. Carbon content in fly and bottom ashes.

	Teruel	**Litoral 1**	**Litoral 2**
Fly ashes (%)	1.05	3.4	5.6
Bottom ashes (%)	0.65	0.78	1.7

4. CONCLUSIONS

Some effects expected in coal combustion, where the calculations are performed using average values, were verified in this work. The main enrichment factor (k) of 4.6 and 6.1, of radioisotopes in fly ashes in relation to coal, was found to be inversely proportional to the ash content in coals (α) (22% and 16% for UPT Teruel and UPT Litoral respectively).

In other measured radionuclides, a relative enrichment in fly ashes, using ^{40}K as radiotracer, was observed. However, this effect is greatly dependent on the measured sample, ranging from 1.5 to 4 in the case of ^{210}Po. This can be due to the lack of correlation between coal and ashes measured in one single instantaneous time. This effect was mainly observed in Litoral CFPP, where the use of imported coals from different countries can present an important variability in radioactive content. So, to obtain enrichment factors that could be used theoretically, it is necessary to perform further measurements. When averages are not considered, enrichments up to 18 for ^{210}Po were found in fly ashes.

For bottom ashes, a small decrease in every radionuclide related to fly ashes was measured, as was expected (Table 3). However, the initial assumption to explain this effect was proved to be erroneous (Table 4). This assumption could be revised considering the behaviour of the different chemical species. For ^{210}Po a decrease in bottom ashes related to fly ashes was measured, exactly as expected.

The use of ^{232}Th as the invariant radioisotope (radiotracer) in ashes to be applied in equation (1) instead of ^{40}K, seems to be a better indicator due to its higher boiling temperature, but needs further verification.

In the gypsum formed in wet desulphuration process, an important concentration was measured in ^{210}Po that can be related to the solubility of the external lead layer formed in fly ashes. This concentration was measured to be greater than a factor 36 (more than 59 if the calculation is made relative to ^{40}K concentration). This effect should be verified in other plants which also use wet desulphuration systems.

Other expected effects, as ^{210}Pb scales formation on heat exchangers, in reducing conditions or, the dependence of specific activity in fly ashes, in relation to particle size, are being object of further investigations.

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