^{210}Pb and ^{210}Po in fossil fuel combustion at the Šoštanj thermal power plant (Slovenia)

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The main aim of the present study was to evaluate ^{210}Pb and ^{210}Po emissions from the Šoštanj TPP and to evaluate their mass balance in unit 4. Samples of coal, fly ash, slag and flue gases were analysed for ^{210}Pb and ^{210}Po content. The results showed that these radionuclides are mostly concentrated in ash (71% and 81% for ^{210}Pb and ^{210}Po, respectively). Only a small part of the input activity was detected in flue gases. The activities of ^{210}Pb and ^{210}Po in unit 4 were from 1.1 to 2.7 Bq m^{-3} and from 0.37 to 0.56 Bq m^{-3}, respectively. The mass balance of the two radionuclides in unit 4 show only 6 and 10 % differences between the annual activities of the input and output samples.

1 Introduction

Coal is one of the most impure fuels. It is largely composed of organic matter but contains also inorganic matter and trace elements that have possible impacts on health. Therefore it causes environmental and technological problems associated with its use. Coal, like most materials found in nature, contains also natural radionuclides. The levels of natural radionuclides in a geological formation depend on its composition and geological history. The average activity concentrations of ^{238}U, ^{232}Th and ^{40}K in coal are 20, 20 and 50 Bq kg^{-1}, respectively [1]. In the production of electric power, coal is burned in a furnace operating at temperatures of up to 1700°C. In the combustion process, volatile radionuclides such as ^{210}Pb and ^{210}Po are partly released in the flue gases and escape to the atmosphere. A significant fraction of the radioactivity is also retained in the bottom ash or slag [2]. The greatest part of the radioactivity in coal remains with the ash but some of the fly ash from coal-fired power plants escapes into the atmosphere. The average radionuclide concentrations in escaping fly ash are 200 Bq kg^{-1} of ^{238}U, 240 Bq kg^{-1} of ^{226}Ra, 930 Bq kg^{-1} of ^{210}Pb, 1700 Bq kg^{-1} of ^{210}Po, 70 Bq kg^{-1} of ^{232}Th and 265 Bq kg^{-1} of ^{40}K [1]. Air pollution in the vicinity of a coal fired thermal power station affects soil, water, vegetation, the whole ecosystem and human health [3].

The Šalek valey is one of the most polluted areas in Slovenia. The biggest polluters are the Šoštanj Thermal Power Plant (TPP), the ash dump, Velenje Coal Mine, the coal deposit, a leather factory and other smaller polluters, traffic, sand production and communal and industrial dumps. All these activities are concentrated in the central part of the valley in an area of about 10 km^2. The Šoštanj TPP with the installed electric power capacity of 745 MW consumes up to 4 million tons of brown coal annually. Šoštanj TPP produces approximately 800 000 t of ash and slag, and approximately 2000 t of fly ash is emitted into the atmosphere with flue gases every year.

2 Experimental

Power plant description. Šoštanj TPP has five separate units. All units have electrostatic precipitators for fly ash removal. Units 4 and 5 also have a wet flue gas desulphurisation system installed. Unit 4 is schematically presented in Figure 1.

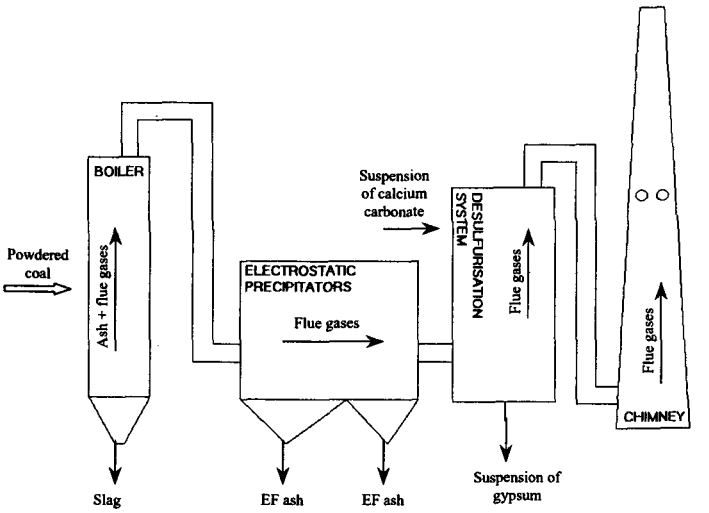

Fig. 1. Schematic representation of Unit 4 at the Šoštanj TPP

Sample collection. All samples were collected during one-day operation of the TPP. Input and output samples from the 4^{th} and 5^{th} units were taken. The input sample was coal, output samples were slag, fly ash from the first and second stage electrostatic precipitators (ESP), and particulate and gaseous phases of the flue gases from the chimneys of units 4 and 5. Equipment for sampling ^{210}Pb and ^{210}Po in flue gas is shown in Figure 2. Flue gas was pumped from the chimney interior through a solid phase trap to prevent fly ash that was not removed by the electrostatic precipitators from entering the bubble traps. ^{210}Pb and ^{210}Po in flue gas is adsorbed in 2 M HCl solution. The flue gas flow rates through the traps were 0.03-0.05 m^3/h. The particles in flue gas were collected isokinetically at a flue gas flow rate of 2.0-2.8 m^3/h in the centre of the gas flow. Filters with particles from flue gas were dried, weighed and leached two times with 8 M HNO_3, evaporated to dryness and then the residue was dissolved in 30-50 mL 2 M HCl. Samples of coal, slag and electrostatic fly ash were dried and sieved through a 0.23mm sieve.

Gamma spectrometry. The activity concentrations of the radionuclides in coal, slag and fly ash were determined by direct γ spectrometry. Dry sample (80 – 100 g) was transferred into a cylindrical polythene vessel. The vessels were hermetically sealed using insulating tape and stored for at least 20 days to allow radioactive equilibrium of the ^{226}Ra series. After that time the samples were measured using the HP Ge detector.

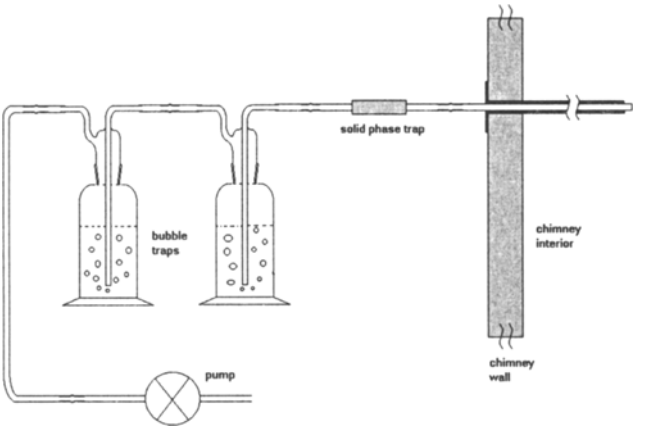

Fig. 2. Equipment for sampling ^{210}Pb and ^{210}Po in the gaseous phase of flue gas

Determination of ^{210}Pb and ^{210}Po. After adding ^{208}Po tracer and 25 mg Pb^{2+} mL^{-1} of lead carrier, samples of coal, electrostatic fly ash and slag were decomposed using 8M HNO_3 and H_2O_2, evaporated to dryness and then the residue dissolved in 30-50 mL 2M HCl. Decomposed samples and samples of flue gases that were collected in 2M HCl were loaded on a Sr resin column (Eichrom Industries Inc.). The analytical method is based on selective separation of lead and polonium by extraction chromatography with bis-4,4'(5')-t-butyl-cyclohexano-18,6-crown ether [4]. The non-retained ions were washed from the column with 100 mL 2M HCl. Polonium was stripped with 6M HNO_3 while lead was removed with 6M HCl solution. A polonium source was prepared by spontaneous deposition of polonium radioisotopes onto a copper disk at 50°C and pH 1 [5,6]. Polonium radioisotopes were then measured by α spectrometry. Lead was precipitated as lead sulphate and the β activity of its daughter ^{210}Bi measured on a β proportional counter [7].

3 Results and discussion

The concentrations of natural radionuclides in input and output samples are presented in Table 1. Table 2 shows activities for ^{210}Pb and ^{210}Po in the solid and gaseous phases of the flue gas. Preliminary results for the mass balance for ^{210}Pb and ^{210}Po in Unit 4 of the Šoštanj TPP were evaluated and presented in Table 3.

The results show that the selected radionuclides are mostly concentrated in ash. The effectiveness of the desulphurization system is reflected in the drop in activities of ^{210}Pb and ^{210}Po in the solid phase of the flue gas. Comparison of the results of this study with a study done in 1998 [8] shows an effective reduction in activities in the solid phase of flue gas from unit 5. In the study from 1998 [8], the average activities of ^{210}Pb and ^{210}Po were 150 ± 15 mBq m^{-3} while the present study showed a decrease in ^{210}Pb values of 5-times (30 mBq m^{-3}), and for ^{210}Po 8-times (average 18 mBq m^{-3}). Average activities of ^{210}Pb and ^{210}Po from unit 4 in both studies are comparable (50 ± 10 mBq m^{-3} for ^{210}Pb

Table 1. Activities of some natural radionuclides in input and output samples from units 4 and 5.

	Unit 4 (Bq kg^{-1})			Unit 5 (Bq kg^{-1})		
Nuclide	Coal	EF Ash	Slag	Coal	EF Ash	Slag
^{238}U	105 ± 10	410 ± 30	340 ± 30	78 ± 6	320 ± 20	230 ± 20
^{226}Ra	92 ± 7	420 ± 40	250 ± 30	85 ± 7	280 ± 30	390 ± 30
^{210}Pb	100 ± 12	420 ± 50	140 ± 17	85 ± 10	490 ± 59	60 ± 7
^{210}Po)	46 ± 4	220 ± 18	32 ± 3	54 ± 4	230 ± 18	28 ± 2
^{232}Th	10 ± 2	44 ± 5	33 ± 5	16 ± 2	72 ± 5	63 ± 5
^{40}K	145 ± 10	570 ± 50	330 ± 30	150 ± 10	680 ± 30	410 ± 30

The results are given as the averages of data on three samples and the error is due to variation among samples.

Table 2. ^{210}Pb and ^{210}Po in solid phase (SP) and in volatilised phases (VP) of flue gas.

Sample		Air volume (L)	Amount of ash (mg)	^{210}Pb (Bq kg^{-1})	^{210}Pb (mBq m^{-3})	^{210}Po (Bq kg^{-1})	^{210}Po (mBq m^{-3})
Unit 4	SP	1990	45.6	1750 ± 210	40 ± 5	760 ± 61	18 ± 1
	VP1	49			2.7 ± 0.3		0.37 ± 0.04
	VP2	40			1.1 ± 0.1		0.56 ± 0.06
	VP3	45			1.9 ± 0.2		0.44 ± 0.04
Unit 5	SP1	2830	25.6	3160 ± 380	29 ± 3	2390 ± 191	22 ± 2
	SP2	2190	11.6	5210 ± 625	28 ± 3	2720 ± 218	15 ± 1
	VP1	30			1.7 ± 0.2		1.7 ± 0.2
	VP2	30			1.1 ± 0.1		1.2 ± 0.1

± counting error

Table 3. Mass balance of unit 4 for ^{210}Pb and ^{210}Po.

	Coal	Slag	EF ash	Flue gas		Dif. (%)
				solid phase	volat. phase	
Annual amount	1571892 t	156948 t	266811 t	158 t	4.5 m^3 kg^{-1*}	
^{210}Pb (Bq/year)	1.57 E+11	2.20 E+10	1.12 E+11	2.77 E+08	1.34 E+10	−5.9
^{210}Po (Bq/year)	7.23 E+10	3.01 E+09	5.87 E+10	1.20 E+08	3.25 E+09	−10

* per kg coal

and 20 ± 2 mBq m^{-3} for ^{210}Po). Activities of ^{210}Pb in the volatile phase of flue gas were from 1.1 to 2.7 Bq m^{-3} in unit 4 and from 1.1 to 1.7 Bq m^{-3} in unit 5. Activities of ^{210}Po in volatile phase of flue gas were from 0.37 to 0.56 Bq m^{-3} in unit 4 and from 1.2 to 1.7 Bq m^{-3} in unit 5. On the basis of these results we evaluated the mass balance of both

radionuclides in unit 4. We considered the annual amounts of coal used and the annual amounts of slag and ash produced. We also considered that from 1 kg of coal we get 4.5 m^3 flue gas. The difference of only 6 and 10 % between the annual activities of the input and output samples from unit 4 shows remarkably good agreement.

4 Conclusions

^{210}Pb and ^{210}Po are volatile radionuclides which are mainly removed from the combustion system of the power plant by the electrostatic precipitators and are mainly found in fly ash (71% and 81% for ^{210}Pb and ^{210}Po, respectively). In spite of that, some of these volatile radionuclides still find their way out through the chimneys into the environment (4.5% and 8.5% for ^{210}Pb and ^{210}Po in the volatile phase respectively). ^{238}U, ^{226}Ra and ^{210}Pb was found to be in radiochemical equilibrium in coal. The desulphurisation system is very effective in reducing the amount of particulate phase in flue gas and the activities of ^{210}Pb and ^{210}Po in these samples and consequently the emissions of selected radionuclides into the environment. The amount of ash was reduced from 40-56 g in 0.6-0.7 m^3 of air volume to 12-26 g in app. 2.2-2.8 m^3 of air volume. The corresponding activities of ^{210}Pb and ^{210}Po in flue gas were reduced 5 and 8-times, respectively. These data are based on a comparison of the results obtained from unit 5 in the study from the year 1998 [8], when the desulphurisation system was not yet installed, and this study. From the mass balance of unit 4 we found only 6 and 10% difference between the annual activities of the input and output samples for ^{210}Pb and ^{210}Po, respectively. Annual emission of ^{210}Pb and ^{210}Po in the volatile phase of flue gas were 1.34×10^{10} Bq and 3.25×10^{9} Bq, respectively.

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