2005 International Nuclear Atlantic Conference - INAC 2005
Santos, SP, Brazil, August 28 to September 2, 2005
ASSOCIAÇÃO BRASILEIRA DE ENERGIA NUCLEAR - ABEN
ISBN: 85-99141-01-5

RADIONUCLIDES CONCENTRATION IN COAL USED IN BRAZILIAN POWER PLANTS

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ABSTRACT

Coal plays an increasingly important role to cover the energy needs of Brazil. Coal represents a major part (66%) of the national energetic resource. Environmental issues are important for the development of new coal-fired power plants. To evaluate the level of coal radioactivity, the concentration of radionuclides present in the raw material were determined. For this research, samples of coal used by the main power plants in Brazil were selected: Presidente Medici, Jacuí and Charqueadas in the State of Rio Grande do Sul (RS); Jorge Lacerda in the State of Santa Catarina (SC); and Figueira in the State of Paraná (PR). Radiological relevant radionuclides of the natural series, such as ^{238}U, ^{232}Th, ^{226}Ra, ^{210}Pb and ^{40}K were analyzed by direct gamma spectrometry. The results of this work showed that the uranium concentration in coal from Figueira (PR) was at least three times higher than concentrations found in other coals samples in Brazil (RS and SC). In spite of the high uranium concentration in the PR coal, the small (10Mwe) local power plant currently operating in Figueira (PR) is not expected to cause significant increase in the natural radioactivity levels of the region. However, more detailed studies should be done for the new power plant (140MWe) in project. As for the SC power plant, the uranium concentration in coal is not so high but the amount of waste ash produced suggests a more detailed environmental study.

1. INTRODUCTION

Coal plays an increasingly important role to cover the energy needs of Brazil, representing 66% [1] of the national energetic resource. Environmental issues are important for the development of new coal-fired power plants. The uncontrolled release of coal burning byproducts can increase the concentration of toxic metals and radionuclide in the environment, therefore the evaluation of the amount of radioactivity in coal is important.

During the seventies and eighties Brazilian coal distribution and occurrence were evaluated. The coal deposits are concentrated in South of Brazil 90.9% in Rio Grande do Sul State (Candiota coalfield is the largest one with 8 billion t), 8.5% in Santa Catarina State, 0.5% in Paraná State and only 0.04% in São Paulo State [2].

The radioactivity of components of the earth's crust is due mostly to the presence of ^{40}K and the radionuclides that form the three natural radioactive series (^{238}U, ^{235}U and ^{232}Th). These radionuclides are distributed uniformly and their variations depend on the rock type. The average concentration of ^{238}U, ^{232}Th and ^{40}K in coal is estimated to be 20, 20 and 50 Bq kg^{-1}, respectively, based on analysis of coal samples from 15 countries, with a variation of more than two orders of magnitude [3].

The increase in specific activities of naturally occurring radionuclides in combustion products, flyash and bottom ash, compared to that of the original coal, depends primarily on the inorganic fraction of the coal (ash content), and can increase the radioactivity in the environment causing a radiological impact. Eisenbud and Petrow [4] first pointed out that the radiation dose from the use of fossil fuel for power generation could be a significant addition to the natural radiation dose.

According to UNSCEAR [5] published data, the annual collective effective equivalent dose to public estimated for the coal combustion cycle was approximate 54.000 man Sv year^{-1}. The world nuclear energy generation caused collective effective equivalent dose to public of 200 man Sv GWe^{-1}. Considering that the world nuclear energy generation in 1987 was 189 GW year^{-1}, the annual collective effective equivalent world dose to public was 37.800 man Sv year^{-1}. This data showed that coal energy generation could cause effective collective equivalent doses that need attention. Therefore doses produced by uranium and thorium present in coal cannot be ignored and need more detailed studies about the concentration of radionuclides in coal used in coal plants.

Although several papers have been published concerning to radioactivity in coal around the world [6,7,8,9], Brazil has few data published so far about the radioactivity in their main coal mines.

The purpose of this study was to evaluate the radioactivity concentration of coal from the main Brazilian coal mines and to estimate the radiological environmental impact due to the operation of the coal power plants. The results obtained will also give information concerning environmental issues due to the upgrade of the coal-fired power plants from Figueira.

2. EXPERIMENTAL PART

To evaluate the level of radioactivity of the Brazilian coals, ^{238}U, ^{226}Ra, ^{210}Pb, ^{232}Th and ^{40}K contents were determined in ROM coal samples (coal run of mine, without treatment) from the beds Candiota, Iruí and Leão/Butiá Mines, in Rio Grande do Sul State (RS); São Geraldo Mine – Siderópolis, in Santa Catarina State (SC); and Cambuí Mine, Figueira, in Paraná State (PR). A pulverized coal of Figueira power plant (PR) was also measured. These coals are used as fuel in the thermoelectric plants Presidente Médici, São Jerônimo and Charqueadas, in Rio Grande do Sul; Jorge Lacerda, in Santa Catarina; and Figueira in Paraná.

All 16 samples of coal analyzed were ground to 200 mesh, homogenized, air dried and hermetically sealed in a cylindrical polyethylene vessel of 5cm diameter and 5.5cm height. ^{238}U, ^{226}Ra, ^{210}Pb, ^{232}Th and ^{40}K contents were measured by gamma spectrometry, with a coaxial germanium detector, EGNC 15-190-R, from Eurisys, with a relative efficience of 15% for the photopeak of ^{60}Co at 1332 keV. The detector was calibrated using standard soils with radionuclides activities certified by Amersham. The samples were sealed for about four weeks prior to the measurement in order to ensure that equilibrium has been reached between ^{226}Ra and its decay products of short half-life. The ^{226}Ra activities were determined by taking the mean activity of three separate photopeaks of its decay product radionuclides: ^{214}Pb at 295.2 keV and 351.9 keV, and ^{214}Bi at 609.3 keV. The ^{232}Th content of the samples was determined by measuring the intensities of the 911 keV and 968 keV gamma-ray peaks of ^{228}Ac, the intensity of the 238 keV gamma-ray peak of ^{212}Pb and the intensity of the 583 keV gamma-ray peak ^{208}Tl. ^{40}K content was measured by the 1460 keV gamma-ray peak. The concentration of ^{210}Pb was carried out by measuring the activity of its low energy peak (46.5 keV) and that of ^{238}U by measuring the ^{234}Th photopeak at 63.3 keV. Self-absorption correction was applied to the low energy peaks (^{210}Pb and ^{234}Th), since the attenuation for low energy gamma rays is highly dependent upon sample composition. The self-absorption factor was calculated by the method suggested by Cutshall, Larsen and Olsen, [10].

The total metal content of uranium and lead in pulverized coal was determined by wavelength dispersive X-ray fluorescence spectrometer RIX 3000 (Rigaku Co, Osaka, Japan). Around 0.9g of coal samples were mixed with boric acid (9:1) and grounded carefully to 200 mesh. The powder was pressed with hydraulic press to obtain a double-layer pressed pellets.

3. RESULTS AND DISCUSSIONS

The results obtained for the activity concentration of ^{238}U, ^{226}Ra, ^{210}Pb, ^{232}Th and ^{40}K in Brazilian coals from different regions (PR, SC, RS) are listed in Table 1. The range obtained for the activity concentration of ^{238}U, ^{232}Th and ^{40}K in ROM Brazilian coals are compared with world coals data from UNSCEAR [11]. The results obtained in this study, present higher concentrations for natural uranium series (from 18 - 874 Bq kg^{-1}) and for ^{40}K (from 181-584 Bq kg^{-1}) compared to the world range for ^{238}U 10-600 Bq kg^{-1}and for ^{40}K 30-100 Bq kg^{-1} [12]. The radionuclide ^{232}Th, on the other hand, is present in low concentrations compared to the world range 10-200 Bq kg^{-1}. The uranium and lead X-ray fluorescence technique evaluation of coal showed average value of 1016±230 Bq kg^{-1} and 80±20 mg kg^{-1}, respectively.

The ^{238}U/^{232}Th ratio for coal around the world was calculated using data from UNSCEAR 1988, for the majority of the coal samples this range varied between 1 and 3.5. Some world coals showed higher ^{238}U concentration with ^{238}U/^{232}Th ratio ranging from 5 to 33 (examples: coal from Austria, Greece, Hungary and Yugoslavia (UNSCEAR [11]). The observed ratio for Brazilians coals from RS and SC (Table 1) showed normal world values, but PR coal showed higher values (^{238}U/^{232}Th ratio around 16 for ROM coal and 35 for pulverized coal).

From the results presented in Table 1, it can be concluded that the coal from PR showed the highest concentration among the Brazilian coals. The ROM coal is grounded and washed to separate the pyrite fraction, before its use in the power plant. The pulverized coal of PR was measured and the uranium series concentration showed an increase by a factor of around 3. Thorium series and ^{40}K had smaller enrichment factor, about 1.5 and 1.6, respectively. This factor suggests that uranium and thorium series are distributed differently in coal and probably have different geochemical properties.

Table1: ^{238}U, ^{226}Ra, ^{210}Pb, ^{232}Th and ^{40}K concentration in Brazilian Coal (Bq kg^{-1})

	^{238}U	^{226}Ra	^{210}Pb	^{232}Th	^{40}K
ROM-PR					
average	356±304	321±199	808±650	22±7	191±77
range	159-807	135-698	249-1745	15-32	136-245
ROM-SC					
average	139±70	98±32	340±328	58±36	556±584
range	42- 181	42-144	91-712	36-100	389-584
ROM-RS					
average	41±15	31±4	75±30	26±5	267±144
range	18 - 48	27-35	41-98	20-30	181-433
Pulverized Coal	Figueira-PR				
average	1111±183	995±178	2252±283	32±8	313±84
range	882-1325	813-1251	1859-2609	24-41	200-450

The ratios ^{238}U/^{226}Ra and ^{210}Pb/^{226}Ra, for uranium series in ROM and pulverized coal was calculated considering the data of Table 1. The average ratio for ^{238}U/^{226}Ra in pulverized and ROM coal were 1.2±0.2 and 1.1±0.2, respectively. These values suggest an approximate equilibrium between the parents and the Ra isotopes in the uranium series, in coals from different locations. If the results of the ratio ^{210}Pb/^{226}Ra (average values of 2.3±0.2 and 2.6±0.9 in pulverized and ROM) are taken into account, it is seen that there is not a secular equilibrium in the decay series, probably due to emanation of ^{222}Rn that migrated into or out of the coal seam, the half time of ^{222}Rn is short (3.8 days) and decays to ^{210}Pb. These appear to represent atypical situation, generally ignored in most assessments. Similar behavior was also found in few reports [9,13,14].

The Pearson correlation matrix ($p<0.05$) for all radionuclides in the ROM and pulverized coal showed a good correlation ($r>0.80$) for the uranium series. The correlation between ^{210}Pb and stable Pb showed a very poor correlation ($r\sim0.1$), suggesting that ^{210}Pb and stable Pb occurrence in coal have different minerals origin. The ^{238}U concentration in the pulverized coal obtained by gamma spectrometry was compared with the uranium concentration obtain by wavelength dispersive X-ray fluorescence spectrometry (XRF) for the same samples. The ratio $^{238}U/U_{XRF}$ was around 1.1, with very good correlation ($r\sim0.90$). These values confirm that both techniques are suitable for the U determination.

In order to estimate the amount of radioactivity present in the waste produced by the coal power plant in Brazil, data concerning capacity, coal consumption, ash content, enrichment factor and ash production for each power plant in Brazil are presented in Table 2. The data concerning capacity, coal consumption and ash content were taken from literature [1] and the enrichment factor was calculated by taking into account the average ash content of each coal.

Table 2; Brazilian power plants capacity, coal consumption and ash content from (SUMÁRIO MINERAL-DNPM; 1999)[1]

Power Plant	Capacity MWe	Coal consumption ($x10^3$ t $year^{-1}$)	Ash content (%)	Enrichment factor (EF)	Ash production $x10^3$ t $year^{-1}$
RS			Average:~ 50% Range: 40-57%	2	
Charqueadas	72	432			216
Pres. Médici	446	2676			1338
São Jerônimo	20	120			60
Total	**538**	**3228**			**1614**
SC			Average: 35% Range: 40-30%	3	
Jorge Lacerda	857	5142			1543
PR			Average: 25% Range:20-30%	4	
Figueira	10	60			15

The activity concentration present in the ashes produced in the Brazilian power plants was calculated multiplying the enrichment factor (EF) presented in Table 2 by the activity concentration of each radionuclide (Table 1) in the coal of the locations studied. The results for the activity concentration of ^{238}U, ^{226}Ra, ^{210}Pb, ^{232}Th, and ^{40}K (Bq kg^{-1}) and the total activity in ash produced by coal power plants of Brazil are presented in Table 3. It can be seen that the ash produced by the PR coal plant is more radioactive (by a factor up to 17) when compared with the other power plants in Brazil. The Brazilian regulatory agency published recently a regulatory guide concerned with the radiological protection of activities which may lead to enhanced concentrations of radionuclides (*Requisitos de Segurança e Proteção Radiológica para Instalações Mínero-industriais* CNEN-NN-4.01) [15]. Such activities may include, for instance, the mining and processing of ores or coal burning as well as storage of raw material, products, by-products, residues and wastes containing radionuclides of the U and Th series, simultaneously or separately, which may incur undue exposures of members of the public and occupationally exposed. All the power plants studied present in their ashes activity contents below 10 Bq g^{-1}, limit adopted by the regulation for category III. These values should exempt such installations from further control by the Brazilian regulatory agency, if the doses to the public and to the workers occupationally exposed are below 1 mSv per year.

The total annual activity present in the ashes for RS, SC and PR power plant was evaluated by taking into account the amount of ashes produced per year (Table 2) and the ash radioactive concentration (Table 3). The results are presented in Table 4. Beck (1989) reported that old power plant released about 10% of fly ash to the environment and 90% were considered waste ash. Ash waste is a mixture of bottom ash and fly ash caught by the filter equipment. This information was used to calculate the amount of waste ash generated by the power plants of RS, SC and PR; and the results are listed in Table 4. The total amount of waste ash (90%) produced by the power plant showed that the SC power plant generate the highest amount of ash waste (2938 GBq $year^{-1}$) and PR power plant the lowest amount (89 GBq $year^{-1}$).

Table 3: Activity concentration of ^{238}U, ^{226}Ra, ^{210}Pb and ^{232}Th and total activity in ash produced by coal power plants of Brazil (Bq kg^{-1}).

	RS-Ash	SC-Ash	PR-Ash	PR*-Ash
^{238}U	82	417	1424	2222
^{226}Ra	62	294	1284	1990
^{210}Pb	150	1020	3232	4504
^{232}Th	52	174	88	60
Total	**346**	**1905**	**6028**	**8776**

PR* ash produced from pulverized coal

Table 4 Total annual activity in the ashes of RS, SC and PR power plant (GBq $year^{-1}$).

	RS ash production GBq $year^{-1}$	SC ash production GBq $year^{-1}$	PR ash production GBq $year^{-1}$
^{238}U	132	643	21
^{226}Ra	100	454	19
^{210}Pb	242	1573	48
^{232}Th	84	268	1.3
Total	**593**	**2938**	**89**

The evaluation of the total radioactivity in ash produced by the PR power plant of Figueira (Table 3) showed that the coal used in this power plant is 3 times more radioactive than the coal from SC and can be a potential problem for the surrounding environment. Luckily, the current power plant in Figueira is a small one (10MWe) and so the amount of ash production is low. However, since a bigger power (140MWe) is in project, a more detailed study of the environmental impact should be carried out. The analyses of the total annual radioactivity in ash waste (Table 4) indicated that the largest power plant of the State of SC causes the largest radiological impact, producing 2938 GBq $year^{-1}$ of radioactive ash. Therefore, in this case also, an environmental impact study is advisable.

4. CONCLUSIONS

The results obtained in this work showed that the uranium concentration in coal from Figueira (PR) was at least three times higher than concentrations found in other coals samples in Brazil (RS and SC). In spite of the high uranium concentration in the PR coal, the small (10Mwe) local power plant currently operating in Figueira (PR) is not expected to cause significant increase in the natural radioactivity levels of the region. However, more detailed studies should be done for the new power plant (140MWe) in project. In the case of SC power plant the uranium concentration in coal is not so high but the amount of waste ash produced suggests a more detailed environmental study.

REFERENCES

1. SUMÁRIO MINERAL 1999 - Ministério de Minas e Energia - Departamento Nacional de Produção Mineral (DNPM) V.14,1999. (ISSN 0101 2053)
2. Anuário Mineral Brasileiro 2001 Ministério de Minas e Energia - Departamento Nacional de Produção Mineral (DNPM) p199.
3. United Scientific Committee on the Effects of Atomic Radiation (UNSCEAR), 1982. "Ionizing Radiation: Sources and Biological Effects". New York: United Nations.
4. Eisenbud, M., Petrow, H.G.. „Radioactivity in the atmospheric effluents of power plants that use fossil fuels". *Science* **144**, pp.288–289, 1964.
5. United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR), 1993."Sources and Effects of Ionizing Radiation", New York: United Nation.
6. Varinlioglu,A.; Akyuz,T.; Kose A. "Natural and artificial radionuclides in selected lignites from Istambul". *J.Radioanal. and Nuclear Chem.,* **246,** pp.391-394, 2000.
7. Alvarez ,M.C.A and Vivero,M.T.D."Natural radionuclide contents in Spanish coals of different rank". *Fuel* . **77**, pp. 1427-1430, 1998.
8. Ayçik,G.A. and Ercan,A. "Radioactivity measurements of coal and ashes from Coal-fired Power Plants in the southwestern part of Turkey". *J.Environ.Radioactiv*. **35,** pp.23-35, 1997.
9. Papastefanon,C.; Charalambous S. "On the escaping radioactivity from coal power plants". *Health Physics* **46**, pp. 293-302, 1984.
10. Cutshall,N., Larsen,I.; Olsen,C. "Direct analysis of ^{210}Pb in sediments samples, selfabsortion corrections".*Nuclear Instrum. and Methods* **206**, pp.309-312, 1983.
11. United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR), 1988."Sources, Effects and Risks of Ionizing Radiation", New York: United Nation.
12. Beck,H.I."Radiation exposure due to fossil fuel combustion".*Radiat.Phys.Chem*.**34**, pp.285-293,1989.
13. DeSantis,V, Longo,I. "Coal energy vs Nuclear energy- Comparison of the radiological risks" *Health Phys.* **46**, pp.73-84, 1984.
14. Kaakinen,J.W., Jorden,R.M.,Lawasani,M.H.,"Trace-elements behavior in a coal-fired power-plant" *Environ.Sci.Technol.,***9,** pp. 862-868, 1975.
15. CNEN-NN 4.01 "Requisitos de Segurança e Proteção Radiológica para Instalações Mínero-industriais"