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ASSESSMENT OF NATURAL RADIOACTIVITY LEVELS IN FLUE GAS DESULFURIZATION GYPSUM AND CLINKER SAMPLES

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ABSTRACT

Coal Combustion Products (CCPs) are the by-products generated from burning coal in coal-fired power plants. which includes fly ash, bottom ash, boiler slag and flue gas desulfurization wastes. These by-products contain trace quantities of naturally occurring radionuclides from the uranium and thorium series, as well as other naturally occurring radionuclides such as ^{40}K derived from the original coal matrix that tend to become enriched in the ashes. Flue gas desulfurization gypsum (FGD gypsum) is the hydrated calcium sulphate produced when SO_x is removed from gases produced during the combustion of coal. FGD gypsum can be used as an alternative material to natural gypsum as retarder additive for Portland cement. In this work, analysis of the radioactive content in FGD gypsum samples were performed to determine if beneficial uses of this CPP in building materials could be of radiological concern. Analysis of clinker sample was also performed. The FGD gypsum samples were collected at Presidente Médici thermoelectric power plant, located in Candiota, RS. The radioactive content of ^{238}U, ^{232}Th, ^{226}Ra, ^{228}Ra, ^{210}Pb and ^{40}K was determined using Neutron activation analysis and Gamma-ray spectrometry. The specific activities (Bq kg^{-1}) were compared to results from literature studies including different building materials and coal ashes specific activities.

1. INTRODUCTION

Coal, the most abundant natural resource and fossil fuel, plays an important role in electricity generation, and approximately 27% of the world's energy consumption originates from the incineration of coal. In Brazil, coal represent 4.45 % of the national production of electricity.
Coal, like most materials found in nature, contains the natural radionuclides ^{238}U, ^{232}Th and ^{40}K. In the process of coal combustion, the mineral material in coal is converted into different by-products (ashes). The concentrations of these radionuclides are usually low in the coal, but enriched in ashes, up to 10 times their original levels [1-2].
FGD gypsum is generated in coal-fired power plant and is a wet sludge produced by flue gas desulfurization units to reduce sulfur dioxide emissions. The gases are desulphurised with an injection of a lime or limestone suspension. The product that is initially formed by gas desulphurization is calcium sulphite. This, by forced oxidation, turns into calcium sulfate dihydrate ($CaSO_4$•$2H_2O$), initially in the form of a suspension. Further a separation of the solid phase takes place through centrifugation or vacuum filtration.
FGD gypsum may be used in wallboard (i.e., drywall) as a full substitute for mined gypsum because the primary chemical constituent, calcium sulfate dihydrate, is identical in both materials. FGD gypsum may contain also some impurities, mainly fly ash [3-5].
In addition, to these forms of radiation, most building materials of terrestrial origin, like clinker, contain small amounts of natural radionuclides. The most important of natural

radionuclides are ^{40}K and members of two natural radioactive series, which can be represented by the isotopes ^{226}Ra and ^{232}Th [6]. The presence of these radioisotopes in the building materials causes external exposure to the inhabitants and can also cause internal exposure due to the concentration of radon and of its daughters [7-8].
Thus, the characterization and quantification of the natural radioactivity contents in construction materials are essential for the subsequent estimation of the associated environmental and health hazards [9-11].
In the present work, radiation characterization was performed for FGD gypsum and clinker to assess the possible radiological risks to human health due to the use of such materials for building construction.

2. MATERIALS AND METHODS

2.1. Materials

All the reagents used for experimental studies were of analytical grade. The FGD gypsum sample was collected at Presidente Médici thermoelectric power plant, located in Candiota, RS. Clinker was supplied by Brazilian Portland Cement Association - ABCP.

2.2. Neutron Activation Analysis

Neutron activation analysis was used to determine the concentrations of the elements U and Th. For this determination, approximately 100 mg of the sample were weighted and packed in polyethylene bags and irradiated in the IEA-R1 nuclear research reactor, at IPEN, in a neutron flux of 10^{12} n cm^{-2}s^{-1} for a period of 8 hours. Reference materials USGS STM-2, NIST SRM 1646a and a paper filter pipetted with a standard solution of the interest elements were also prepared and irradiated together with the samples to calculate the concentrations by the comparative method.
After the irradiation, two sets of measurement were done. The first, after a one week period of cooling, to determine U concentrations and, the second, after two weeks, to determine Th concentration. Samples were counted for a period of 5000 s, in the first and second measurement, by using an EG&G Ortec Ge high pure Gamma Spectrometer detector (AMETEK Inc., USA) and associated electronics, with a resolution of 0.88 and 1.90 keV for 57Co (122 keV) and 60Co (1332 keV), respectively [12]. Activity concentrations of U and Th were obtained by their specific activity using the conversion factor of 24.5 and 4.05, respectively.

2.3. Gamma Spectrometry

The concentration of the natural radionuclides ^{226}Ra, ^{228}Ra, ^{210}Pb and ^{40}K were carried out by non-destructive γ-ray spectrometry. Samples were packed in 50 cm^3 polypropylene cylindrical containers and they were kept sealed for at least 30 days in order to reach radioactive equilibrium between ^{226}Ra and ^{222}Rn progenies.
A HPGe EG&G Ortec detector with 40% of relative efficiency and 2.09 keV resolution at 1.33 MeV and associated electronic devices were used, with live counting time of 80,000 s.

The spectra were acquired by multichannel analyzer and, for the analysis, Genie 2000 software package was used. The activity concentration for ^{210}Pb in the samples was corrected for self-absorption according to the method described in [13]. The detector efficiency was calibrated by using the reference material IAEA-RGU-1, IAEA-RGTh-1 and IAEA-RGK-1.

3. RESULTS AND DISCUSSION

In the production of raw Portland cement, the heating of a homogeneous mixture of raw materials, mainly limestone and various clays, will produce clinker. The clinker consists of various calcium silicates, tricalcium aluminate, and calcium aluminoferrite. Once the clinker lumps have cooled, approximately 5% gypsum is added and then the combined materials are ground into a fine powder [14].

The gypsum plays a very important role during the cement manufacturing process. The introduction of gypsum (natural or synthetic) is used to control the set time of the cement. If not added, the cement will set immediately after mixing of water leaving no time for concrete placing [14].

The results obtained for the activity concentration of ^{238}U, ^{226}Ra, ^{210}Pb, ^{228}Ra, ^{232}Th and ^{40}K in the FGD gypsum and clinker are listed in Table 1 (average of measured activity values together with their respective standard deviation).

Table 1: Activity concentrations of FGD gypsum and clinker (in Bq kg^{-1})

	^{238}U	^{232}Th	^{226}Ra	^{210}Pb	^{228}Ra	^{228}Th	^{40}K
Clinker	20 ± 1	11.5 ± 0.5	21 ± 1	49 ± 9	11.0 ± 0.5	11 ± 1	280 ± 13
FGD	50 ± 6	38 ± 2	28 ± 3	117 ± 22	26 ± 1	36 ± 2	161 ± 9

In both samples (Table 1), the radionuclide with the highest activity concentration was ^{40}K, followed by ^{210}Pb.

^{210}Pb is a product of the ^{238}U decay series, derived via a series of other short-lived radionuclides from the decay of gaseous ^{222}Rn ($t_{1/2}$=3.8 days), the daughter of ^{226}Ra ($t_{1/2}$=1,622 years). It is one of the most volatile radionuclide and tends to be enriched on the fly ash particles during coal combustion, thus presenting a high concentration in FGD gypsum. ^{210}Pb is also derived naturally from the lithogenic minerals in subsoil and adheres to clay particles present in soils or in suspended sediments in water bodies [15]

According to standard values published by UNSCEAR [16], the world average concentrations in silicoaluminate fly ashes are 240 Bq kg^{-1} for ^{226}Ra, 70 Bq kg^{-1} for ^{232}Th, 265 Bq kg^{-1} for ^{40}K and 200 Bq kg^{-1} for ^{238}U. Comparing the present results, the FGD gypsum presented lower activity concentration than standard values for all the radionuclides of fly ash.

The average activity concentrations of the radionuclides of natural and synthetic gypsum from different countries all over the world are shown in Table 2 for comparison.

Table 2: Comparison of the average activity concentrations (Bq Kg^{-1}) of synthetic and natural gypsum in published data

^{238}U	^{232}Th	^{40}K	^{226}Ra	Reference
9 (1-24)	1 (0.2 -3)	10 (2-19)	-	[17][1]
-	-	13 ± 3	22 ± 3	[18][2]
	91.2 ± 3.8	1101.1 ± 19	58.4 ± 3.7	[9][3]
37.62 ± 20.7	42.27 ± 20.3	499.29 ± 113.58	91.97 ± 48.83	[19][4]
	9 (1-100)	91 (5-279)	15 (1-70)	[20][5]
	-	18.1	6.3	[21][6]

(1) mean (n=20) and range of FGD gypsum; (2) value ± deviation of FGD gypsum; (3) mean ± standard deviation (n=3) of natural gypsum from India; (4) mean ± standard deviation (n=18) of natural gypsum from Egypt; (5) mean (n=502) and range of natural gypsum from 16 EU member states; (6) mean of natural gypsum from Brazil.

It is important to point out that the values of natural gypsum were not the representative values for the countries but for the regions from where the samples were collected. Radium, thorium and potassium are not uniformly distributed in soil or rocks, from which building materials are derived, but the radioactivity varies, over some meters. In general, these materials have no require any protection against radiation [22]

In the same way, the concentrations of radionuclides contained in the cement clinker vary according to the region from which the raw material is extracted for its production. Table 3 shows the range concentrations of the ^{232}Th, ^{40}K and ^{226}Ra elements content on clinker for cements produced in different regions [22].

Table 3: Activity concentrations of ^{232}Th, ^{40}K and ^{226}Ra elements content on clinker (in Bq kg^{-1})

^{232}Th	^{40}K	^{226}Ra	Country
18.4 ± 3,7	156.5 ± 101	11.8 ± 9.0	Slovak Republic[1]
48.1	114.7	51.8	Australia
14.2	210	26.7	Austria
80	1133	61	Bangladesh
58.5	564	61.7	Brazil
32	207.7	51.7	China
19	93	35	Egypt
19,9	251	40.2	Finland
31	310	92	Greece
42	316	46	Italy
21	139	36	Japan
59,2	203.5	81.4	Malaysia
19	230	27	Netherlands
18.5	259	29.6	Norway
28.7	272.9	26.1	Pakistan
26	267	41	Turkey

(1) mean ± standard deviation

The specific activities of ^{226}Ra, ^{232}Th and ^{40}K in the cement according to the European Commission report are 40, 30, and 400 Bq kg^{-1}, respectively [23]. Thus, besides that its own radiological character of raw cement, the adding of coal fly ash can cause a non-negligible increase in its radioactivity content. In the present study, FGD gypsum presented a low content of natural radionuclides.

4. CONCLUSIONS

Materials that are locally produced and used for the construction of buildings were examined to assess their radioactivity levels. The natural radionuclide content of the ^{238}U, ^{232}Th, ^{226}Ra, ^{228}Ra, ^{210}Pb and ^{40}K in the FGD gypsum and clinker samples from Brazil were measured by using the technique of Neutron Activation Analysis and Gamma-ray Spectrometry. The activities are compared with available reported data from other countries. The contents of naturally occurring radioactive material (NORM) in clinker materials can vary considerably depending on their chemical composition in relation to geological source and geochemical characteristics. In general, not enough data were available for by-products of industrial origin used in building materials, mainly for FGD gypsum, so, comparative evaluation is not possible. The data obtained are essential for development of standards and guidelines concerning the use and management of building materials in Brazil.

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REFERENCES

[1] Marija M. Janković, Milica M. Rajačić, Dragana J. Todorović,Nataša B. Sarap, Jelena D. Nikolić, Gordana K. Pantelić, Milanka M. Krstić. “Study of Radioactivity in Environment around Power Plants TENT A and KOLUBARA due to coal burning for 2015”. *RAD Conference Proceedings*, **vol.1**, pp.84-89. (2016).

[2] Pandit, G.G., Sahu, S.K. and Puranik, V.D. “Natural radionuclides from coal fired thermal power plants – estimation of atmospheric release and inhalation risk”. ICRER 2011 – International Conference on Radioecology & Environmental Radioactivity: *Environment & Nuclear Renaissance*, **vol.46**. pp.173-179. (2011).

[3] Castro, R. de P. V. *Caracterização de sólidos e desenvolvimento de metodologia analítica para monitoramento de tratamento oxidativo de de resíduos sólidos de dessulfurização de gases exaustos de termoelétrica a carvão*. Dissertação de Mestrado. Universidade Federal do Rio de Janeiro. 2016.

[4] Ramme, B. W.; Tharaniyil, M. P. *Coal combustion products utilization handbook*. We Energies Publication, Wisconsin Electric Power Company. Third Edition. Milwaukee, Wisconsin, EUA. <www.we-energies.com>. (2013).

[5] Srivasta, R. K. “Controlling SO_2 emissions: a review of technologies”. *U.S. Environmental Protection Agency - EPA*. Washington, D.C. <https://cfpub.epa.gov>. (2000).

[6] Kovler K. “The national survey of natural radioactivity in concrete produced in Israel”. *Journal of Environmental Radioactivity*. **vol.168**. pp.46-53. (2017).

[7] G. Keller, K.H. Folkerts, H. Muth. “Discussing possible standards of natural radioactivity in building materials”. *Radiation and Environmental Biophysics*. **vol.26**. pp.143-150. (1987).

[8] A. Savidou, C. Raptis, P. Kritidis. “Study of natural radionuclides and radon emanation in brick used in the Attica region”. *Greece Environmental Radioact.* **vol.31**. pp.21-28. (1996).

[9] Asaduzzaman K, Mannan F, Khandaker MU, Farook MS, Elkezza A, Amin YBM, et al. “Assessment of natural radioactivity levels and potential radiological risks of common building materials used in Bangladeshi dwellings”. *PLoS ONE10*. <doi:10.1371/journal.pone.0140667>. (2015).

[10] Rahman SU, Rafique M, Jabbar A, Matiullah. “Radiological hazards due to naturally occurring radionuclides in the selected building materials used for the construction of dwellings in four districts of the Punjab province, Pakistan”. *Radiation Protection Dosimetry*. **vol.153(3)**. pp.352–360. 2013.

[11] Khandaker MU, Jojo PJ, Kassim HA, Amin YM. “Radiometric analysis of construction materials using HPGe gamma-ray spectrometry”. *Radiation Protection Dosimetry*.; **vol.152**. pp.33-37. (2012).

[12] IAEA - International Atomic Energy Agency. *Practical aspects of operating a neutron analysis laboratory*. IAEA – **TECDOC- 564**. 252p. Vienna. (1999).

[13] Cutshall, N. H.; Larser, I. L.; Olsen, C. R. “Direct analysis of ^{210}Pb in sediment samples: self-absorption corrections”. *Nuclear Instruments and Methods*, **vol.206**. pp.309-312. (1983).

[14] ACAA - American Coal Ash Association. *Synthetic Gypsium: Beneficial Uses for Construcution and Agriculture*. <https://www.acaa-usa.org/Portals/9/Files/PDFs/ASH01-2016.pdf>. (2016).

[15] Uğur A, Ozden B, Yener G, Saç MM, Kurucu Y, Altinbaş U, Bolca M. “Distributions of ^{210}Pb around a uraniferous coal-fired power plant in Western Turkey”. *Environmental Monitoring Assessment*. **vol.149**. pp.195-200. (2009).

[16] UNSCEAR - United Nations Scientific Committee on the Effects of Atomic Radiation. *Sources and effects of ionizing radiation*. UNSCEAR Report 2000, **vol.1- annex b**. (2010).

[17] Roper. A. R. *Analysis of naturally occurring radionuclides in fly ash and gypsum samples*. Master of Science. Vanderbilt University. (2012).

[18] Kardos, R., Sas, Z., Hegedus, M., Shahrokhi, A., Somlai, J., & Kovacs, T. “Radionuclide content of NORM by-products originating from the coal-fired power plant in Oroszlány (Hungary)”. *Radiation Protection Dosimetry*. **vol.167(1-3)**. pp.266-269. <https://doi.org/10.1093/rpd/ncv259>. (2015).

[19] Korna, A.H.; Fares, S.S.; El-Rahman, M.A. "Natural radioactivity levels and radiation hazards for gypsum materials used in Egypt". *Natural Science*. **vol.6**. pp.5-13. (2014).

[20] Trevisi R, D'Alessandro M, Risica S and Nuccetelli C. "Natural radioactivity in building materials in the European Union: a database and an estimate of radiological significance" *Journal of Environmental Radioactivity*. **vol.105**. pp.11–20. (2012).

[21] NEA-OECD, Nuclear Energy Agency. *Exposure to radiation from natural radioactivity in building materials*. Report by NEA Group of Experts. OECD. Paris. (1979).

[22] Eštoková, A.; Palaščáková, L. "Assessment of natural radioactivity levels of cements and cement composites in the Slovak Republic". *International Journal of Environmental Research Public Health*. **vol.10(12)**. pp.7165-7179. (2013).

[23] Commission European. *Radiological protection principles concerning the natural radioactivity of building materials*. **Radiation Protection 112**. pp.1–16. (1999).