Natural radionuclides content and radon exhalation rate from Brazilian phosphogypsum piles

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Abstract. Phosphogypsum is a waste of the wet-acid process for producing phosphoric acid from phosphate rock. For every ton of phosphoric acid obtained, from the reaction of phosphate rock with sulfuric acid, about four tons of phosphogypsum are produced. The level of radioactivity present in the phosphogypsum, among other impurities, prevents its reuse for a variety of purposes. Large quantities of phosphogypsum have been produced worldwide. In 2006, the annual production was estimated to be about 170 million tons. Brazilian annual production of phosphogypsum reaches 5.5 million tons. Brazil, like other countries that produce phosphate fertilizer, tries to find solutions for the safe applications of phosphogypsum, in order to minimize the impact caused by its disposal. Most of the worldwide phosphogypsum is stockpiled, posing environmental concerns. The monitoring of air and groundwater pollution, radon exhalation rate and direct exposure to gamma radiation for workers should be considered. The aim of this study is to evaluate the natural radionuclides content and the radon exhalation rate from phosphogypsum piles from Ultrafertil and Fosfertil fertilizer industries. Samples of this material were analyzed by gamma ray spectrometry for their radionuclide content. Radon exhalation rate was measured by the activated charcoal collector method. A theoretical model for radon exhalation calculation, suggested by UNSCEAR, was applied in order to corroborate the experimental results.

Keywords: Phosphogypsum - radon exhalation rate - activated charcoal collector - gamma-ray spectrometry.

1 Introduction

The ^{222}Rn is formed as a product of the radioactive decay series of ^{238}U from the alpha decay of ^{226}Ra. It can diffuse through the soil and building materials and concentrates indoors. Apart from the soil and building materials [1,2], mineral waters and springs are important sources of ^{222}Rn [3]. The concentration of radon in an environment depends primarily on the exhalation of gas through the soil and building materials. The exhalation rate is defined as the amount of activity released per unit surface area per unit time from the material. It depends on the ^{226}Ra content of the material, emanation factor, gas diffusion coefficient in material, porosity and density of the material [4-6].

Materials containing natural radionuclides can be classified as Naturally Occurring Radioactive Materials - NORM, or Technologically Enhanced Naturally occurring Radioactive Material - TENORM, depending on if there was or not an industrial processing that could lead to increased concentration of radionuclides in the material. Phosphogypsum, a waste of the fertilizer industry, can be classified as TENORM. It is obtained in the wet-acid processing of phosphate rock to produce phosphoric acid. For every ton of phosphoric acid produced in the reaction of phosphate rock with sulphuric acid, about four to five tons of phosphogypsum are produced. The Brazilian production of phosphogypsum reaches 5.5 million tons per year and the major generating industries are located in Cajati and Cubatão, State of Sao Paulo and in Uberaba, State of Minas Gerais [7]. Currently, most of the phosphogypsum produced is stored in outdoor piles, which requires monitoring, checking for possible air pollution, groundwater pollution, radon exhalation and direct exposure to gamma radiation [8,9]. Most studies were not conclusive regarding the risk that workers are subjected from phosphogypsum stacks [5].

The aim of this study is to evaluate the natural radionuclides content and the radon exhalation rate from phosphogypsum piles from Ultrafertil and Fosfertil fertilizer industries. Samples of this material were analyzed by gamma ray spectrometry for their ^{226}Ra, ^{228}Ra, ^{228}Th, ^{40}K and ^{210}Pb activity concentration. Radon exhalation rate was measured by the activated charcoal collector method. A theoretical model for radon exhalation calculation, suggested by UNSCEAR, was applied in order to corroborate the experimental results.

Methodology

Samples of phophogypsum from Ultrafertil and Forsfertil were dried, packed in a polyethylene bottle of 100 ml and sealed for about four weeks prior to measure in order to ensure that radioactive equilibrium had been reached between ^{226}Ra and its progeny. After this time phosphogypsum samples were measured by gamma-ray spectrometry with a hyper-pure germanium detector Canberra model GX2518, 25% relative efficiency, effective resolution of 1.8 keV on the 1332 keV ^{60}Co with associated electronics and coupled to a microcomputer.

The activity concentration of ^{40}K was determined directly by its own gamma-ray peak at 1460.8 keV, while concentrations of ^{226}Ra, ^{228}Ra and ^{228}Th were calculated based on the weighted mean value of their respective decay products in equilibrium. The activity concentration of ^{226}Ra was determined using the 295.2 and 351.9 keV gamma rays from ^{214}Pb and the 609.3 keV from ^{214}Bi. The activity concentration of ^{228}Ra was determined using the 338.4, 911.1 and 968.9 keV photopeaks from ^{228}Ac. The activity concentration of ^{228}Th was determined using the 238.6 and 727.3 keV photopeaks from ^{212}Pb and ^{212}Bi. The activity concentration of ^{210}Pb was determined by its 46.5 keV photopeak. Self-absorption correction was applied due to the low energy gamma ray attenuation by the sample, using the method described by Cutshall et al. [10].

All spectra were analyzed with the Interwinner 6.0 from Eurisys Measurements Incorporation [11] software for personal computer analysis of gamma-ray spectra from HPGe detectors. The background radiation was obtained by measuring water in the same sample geometry used for samples. The counting time was determined from the model proposed by Nisti et al.[12]. The efficiency of counting was determined by measuring for the same polyethylene flask of 100 ml filled with water spiked with standard solution, in a range from 46.5 to 1408 keV. The uncertainty for the concentration of each sample was calculated using propagation of uncertainty. The intensities of gamma transitions were obtained from the literature.

Radon exhalation rate from phosphogypsum piles was determined through the activated carbon adsorption technique. The radon amount exhaled from material was determined through the concentration of ^{214}Pb and ^{214}Bi descendants, obtained by gamma-ray spectrometry [5,13]. The calculation of the floor area of radon adsorption on activated charcoal and exposure time to the phosphogypsum were also considered. A polyethylene bottle of 100 ml with pure activated charcoal granules, ranging in diameter from 6 to 10 mm, with holed lid and tulle were used as collector for radon adsorption. The internal volume of the polyethylene bottle was completely filled with activated charcoal to ensure the retention of coal inside the bottle without affecting the adsorption of ^{222}Rn by the activated charcoal collector, so a covering of tulle was attached to the bung holes. The collectors were placed inside a PVC pipe with a diameter of 7.2 cm, sealed with the PVC pipe cover and installed in four different points in the phosphogypsum piles, thus forming a cumulative radon device. A total of eight sampling points were monitored at both phosphogypsum piles. The sampling time at phosphogypsum piles of Ultrafértil and Fosfertil was 8 and 1.7 days, respectively. After the sampling period, the radioactivity on activated carbon bottles was determined by gamma spectrometry.

After removal, the phosphogypsum stack collector was sealed and stored for 4 hours prior to measure, so that the radioactive equilibrium was reached between ^{222}Rn and its progeny. The activated charcoal collector was measured by gamma-ray spectrometry with the same system described above.

The ^{222}Rn was determined using the 295.2 and 351.9 keV gamma rays from ^{214}Pb and the 609.3 keV from ^{214}Bi.

The determination of the minimum detectable activity (MDA) was made by the model proposed by Currie [14].

In order to check the radon exhalation rate results obtained from the activated charcoal collector, the exhalation rate of ^{222}Rn from Fosfértil and Ultrafértil phosphogypsum piles were also calculated, through the model proposed by UNSCEAR [15]. The radon exhalation rate was determined through the ^{226}Ra concentration from phosphogypsum, the real density and total porosity of phosphogypsum.

Results and discussion

Phosphogypsum samples from Ultrafértil and Fosfertil were analyzed for ^{226}Ra, ^{228}Ra, ^{228}Th, ^{40}K and ^{210}Pb activity concentrations. Tables 1 and 2 present the average results of the concentrations and respective standard deviations. Samples were collected and analyzed in triplicate.

Table 1 Average concentrations of ^{226}Ra, ^{228}Ra, ^{228}Th, ^{40}K and ^{210}Pb (Bq kg^{-1}) from Ultrafértil phosphogypsum.

	Concentrations (Bq·kg^{-1})				
Sampling Point	^{226}Ra	^{228}Ra	^{228}Th	^{40}K	^{210}Pb
1	324 ± 10	262 ± 16	285 ± 11	< 26	433 ± 63
2	316 ± 7	281 ± 3	313 ± 13	< 31	401 ± 27
3	317 ± 7	266 ± 1	277 ± 15	< 32	421 ± 45
4	308 ± 2	267 ± 4	293 ± 7	< 27	397 ± 29

Table 2 Average concentrations of ^{226}Ra, ^{228}Ra, ^{228}Th, ^{40}K and ^{210}Pb (Bq kg^{-1}) in the phosphogypsum stack from Fosfertil.

	Concentration (Bq·kg^{-1})				
Sampling Point	^{226}Ra	^{228}Ra	^{228}Th	^{40}K	^{210}Pb
1	296 ± 7	319 ± 2	218 ± 6	< 41	323 ± 11
2	274 ± 9	305 ± 5	180 ± 5	< 43	300 ± 49
3	357 ± 5	455 ± 13	366 ± 4	< 45	372 ± 5
4	291 ± 12	332 ± 4	227 ± 16	< 49	312 ± 16

Results of radionuclide concentrations of ^{226}Ra, ^{228}Ra, ^{228}Th, ^{40}K and ^{210}Pb in the phosphogypsum piles from Ultrafértil and Fosfértil are in accordance with literature values [7].

The ^{222}Rn exhalation rate from phosphogypsum stacks was calculated through the ^{214}Pb and ^{214}Bi concentrations, considering that the adsorption of ^{222}Rn on activated charcoal collector was constant and with 100% efficiency

[5]; all results were corrected by date of removal of the phosphogypsum piles collector and its exposure period [16]. Table 3 shows the results of the radon exhalation rate from Ultrafertil and Fosfértil phosphogypsum.

Table 3 ^{222}Rn exhalation rate (Bq m^{-2} s^{-1}) from Ultrafertil and Fosfértil phosphogypsum piles

Sampling point	ULTRAFÉRTIL ^{222}Rn (Bq m^{-2} s^{-1})	FOSFÉRTIL ^{222}Rn (Bq m^{-2} s^{-1})
1A	0.102 ± 0.004	0.073 ± 0.003
1B	0.083 ± 0.003	0.070± 0.003
2A	0.214 ± 0.008	0.053 ± 0.004
2B	0.195 ± 0.007	0.051 ± 0.003
3A	0.268 ± 0.010	0.098 ± 0.006
3B	ND	0.091 ± 0.006
4A	0.119 ± 0.005	0.082 ± 0.003
4B	ND	0.115 ± 0.005
mean ±standard deviation	0.164 ± 0.073	0.079 ± 0.022

ND: not determined (sampler damaged)

The bulk and real density and total porosity of phosphogypsum were determined in order to calculate the radon exhalation rate following the UNSCEAR model procedures [17]. Table 4 shows the results of the bulk and real densities, plus total porosities for Ultrafértil and Fosfertil phosphogypsum.

Table 4 Bulk density, real density and total porosity from Ultrafértil and Fosfértil phosphogypsum.

Sampling point	Bulk density (g·cm^{-3})	real density (g·cm^{-3})	total porosity (%)
ULTRAFÉRTIL 1	1.21	2.40	49.6
ULTRAFÉRTIL 2	1.20	2.63	54.4
ULTRAFÉRTIL 3	1.20	2.39	49.7
ULTRAFÉRTIL 4	1.20	2.69	55.4
FOSFÉRTIL 1	0.76	2.64	71.1
FOSFÉRTIL 2	0.76	2.38	67.9
FOSFÉRTIL 3	0.76	2.50	69.6

FOSFÉRTIL 4	0.75	2.50	69.9

The ^{222}Rn radon exhalation in the phosphogypsum piles from Ultrafértil and Fosfértil, through the UNSCEAR model are presented in table 5.

Table 5 ^{222}Rn exhalation rate from phosphogypsum piles of Ultrafértil and Fosfértil, using the UNSCEAR model.

Sampling point	^{222}Rn (Bq m^{-2} s^{-1})
ULTRAFÉRTIL 1	0.161
ULTRAFÉRTIL 2	0.155
ULTRAFÉRTIL 3	0.156
ULTRAFÉRTIL 4	0.152
mean ± standard deviation	0.156 ± 0.004
FOSFERTIL 1	0.092
FOSFERTIL 2	0.086
FOSFERTIL 3	0.111
FOSFERTIL 4	0.090
mean ± standard deviation	0.094 ± 0.011

The results of ^{222}Rn exhalation rates from phosphogypsum piles of Ultrafértil and Fosfértil, using activated charcoal collectors, were consistent with the values calculated by the UNSCEAR model. The average radon exhalation rate for Ultrafértil, with activated charcoal collectors, was 0.164 ± 0.073 Bq m^{-2} s^{-1} and, by UNSCEAR model, was 0.156 ± 0.004 Bq m^{-2} s^{-1}; for Fosfértil, the average results obtained were 0.079 ± 0.022 Bq m^{-2} s^{-1} (activated charcoal collectors) and 0.094 ± 0.011 Bq m^{-2} s^{-1} (UNSCEAR).

It was demonstrated that the results obtained through the activated charcoal collectors are in accordance with the UNSCEAR model.

It can be pointed that, although the radium activity concentration for Ultrafértil and Fosfertil phosphogysum are similar, the radon exhalation rates are different. This fact can be explained by different porosities of phosphogypsum, indicating that this parameter is strongly related with radon exhalation rate.

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