Natural radioactivity and ^{222}Rn exhalation rate from Brazilian phosphogypsum building materials

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Abstract. Phosphogypsum is classified as a NORM residue and one of the main environmental concerns of its use is the radon exhalation from this material. The aim of this study is to determine the activity concentration of natural radionuclides, radium equivalent activities, external and internal hazard index and the radon exhalation rate from bricks and plates made of phosphogypsum. The activity concentration and radon exhalation rate were in accordance with literature values. The results of radium equivalent, external and internal hazard index showed that plates and bricks from Ultrafertil and Fosfertil presented values above the recommended limits; indicating the necessity of using more realistic models for the safe application of phosphogypsum as building materials. The results of this study can contribute for the establishment of guidelines by the Brazilian regulatory agency, for the safe use of phosphogypsum as building material

Keywords: Phosphogypsum, Radon, NORM, Gamma-ray spectrometry, radon exhalation rate.

1. Introduction

Radon is a natural radioactive noble gas that can be found in soil, water, outdoor and indoor air. Exposure to radon accounts for more than half of the annual effective dose from natural radioactivity [1].

Building materials are one of the main radon sources in houses, since they can contain small amounts of natural radioactivity such as ^{226}Ra, ^{232}Th and ^{40}K [2]. The content is usually low, but some materials, like phosphogypsum, may contain higher concentrations depending on the origin of the raw material used [3].

Phosphogypsum is classified as a NORM (Naturally Occurring Radioactive Material) residue and one of the main environmental concerns of its use is the radon exhalation from this material. Phosphogypsum is a residue from the wet-acid process of phosphoric acid production. The Brazilian phosphate industry is responsible for the production of 5.5 million ton per year of phosphogypsum [4].

The radioactivity present in the phosphogypsum, among other impurities, prevents its reuse for a variety of purposes. In Brazil, industries dealing with NORM residues are subjected to the recommendations given by Comissão Nacional de Energia Nuclear (CNEN), which include compliance with the radiological protection regulations [5]. CNEN has also established, recently, the exemption levels of 1000 Bq kg^{-1} of ^{226}Ra and ^{228}Ra for the use of phosphogypsum in agriculture and cement industry [6]. However, there is not yet a specific regulation for the use of PG as a building material.

One possible application of phosphogypsum is in the manufacture of building materials. In this case, one of the major radiological concerns is the radon exhalation from this material. 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 the material, porosity and density of the material [7-9].

Several studies were undertaken in Brazil concerning the radiological impact of using the phosphogypsum as building material [10-15]. An early publication of Mazzilli and Saueia [10] presented the activity concentration of ^{226}Ra, ^{232}Th and ^{40}K in Brazilian phosphogypsum samples and discussed the radiological implications of using it as building materials. In this paper a conservative model was applied to evaluate the external and internal exposure for people living in a hypothetical house made with this material. In order to apply a more realistic model an experimental house was constructed with walls and roof made of phosphogypsum plates from different origins. In this study a comprehensive radiological evaluation was performed, including measurement of the external gamma exposure and radon concentrations. The results showed that the annual increment in the effective dose to an inhabitant of the house was below the 1mSv limit for every reasonable scenario [11-14].

Nisti et al. [15] evaluated the radon exhalation rate from phosphogypsum piles from different phosphate fertilizer industries, by using by the activated charcoal collector method and theoretical model suggested by UNSCEAR [1].

As a complementary study, this paper aims to determine the activity concentration of natural radionuclides, radium equivalent concentration, external and internal hazard indices and the radon exhalation rate from bricks and plates made of phosphogypsum from three Brazilian phosphate fertilizer industries: Ultrafertil, Fosfertil and Bunge. Samples of phosphogypsum bricks and plates were analyzed by gamma spectrometry for their radionuclide content. The radium equivalent activity, external and internal hazard indices and radon exhalation rate were determined using theoretical models. The Figure 1 presents bricks and plates made of phosphogypsum.

FIG. 1. Bricks and Plates made of phosphogypsum.

2. Materials and methods

Samples of phophogypsum were dried for 24 h in an air circulation oven at 60°C, 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 and ^{232}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 ^{232}Th was determined using the 338.4, 911.1

and 968.9 keV photopeaks from ^{228}Ac, the 238.6 and 727.3 keV photopeaks from ^{212}Pb and ^{212}Bi, assuming ^{232}Th – ^{228}Ra equilibrium.

All spectra were analyzed with the Interwinner 6.0 from Eurisys Measurements Incorporation [16] 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. [17]. The determination of the minimum detectable activity (MDA) followed the model proposed by Currie [18], each sample was collected and analyzed in triplicate.

The ^{226}Ra, ^{232}Th and ^{40}K activity concentrations of Brazilian phosphogypsum building materials were used for the calculation of radium equivalent activity and external and internal hazard indices [19].

The radium equivalent activity was obtained by the equation (1):

$$C_{Ra,eq} = C_{Ra} + 1.43 C_{Th} + 0.077 C_K \quad (1)$$

where

$C_{Ra,eq}$ is the radium equivalent activities (Bq kg^{-1}),
C_{Ra} is the activity concentrations of ^{226}Ra (Bq kg^{-1}),
C_{Th} is the activity concentrations of ^{232}Th (Bq kg^{-1}),
C_K is the activity concentrations of ^{40}K (Bq kg^{-1}),
1, 1.43 and 0.077 index values were defined on hypothesis that 370 Bq kg^{-1}, 259 Bq kg^{-1} and 4810 Bq kg^{-1} for ^{226}Ra, ^{232}Th and ^{40}K produce the same gamma ray exposure.

External and internal hazard indices were calculated using the following equation (2) and (3), respectively:

$$\frac{C_{Ra}}{370} + \frac{C_{Th}}{259} + \frac{C_K}{4810} \leq 1 \text{ for external exposure} \quad (2)$$

$$\frac{C_{Ra}}{185} + \frac{C_{Th}}{259} + \frac{C_K}{4810} \leq 1 \text{ for internal exposure} \quad (3)$$

where

C_{Ra} is the activity concentrations of ^{226}Ra (Bq kg^{-1}),
C_{Th} is the activity concentrations of ^{232}Th (Bq kg^{-1}),
C_K is the activity concentrations of ^{40}K (Bq kg^{-1}),
370, 259 and 4810 are the indices for external exposure,
185, 259 and 4810 are the indices for internal exposure.

The radon exhalation rate of ^{222}Rn was determined using a theoretical model proposed by UNSCEAR [1], through the ^{226}Ra concentration. The determination radon exhalation rate used the equation (4).

$$J_D = C_{Ra} \lambda_{Rn} f \rho L \tanh(d / L) \quad (4)$$

where

J_D is the radon exhalation rate of ^{222}Rn (Bq m^{-2} h^{-1}),
C_{Ra} is the activity concentration of ^{226}Ra (Bq kg^{-1}),
λ_{Rn} is the decay constant of ^{222}Rn (h^{-1}),
f is the emanation fraction,
ρ is the density (kg m^{-3}),
d is half-thickness (m),
L is the diffusion length (m^2).

3. Results and discussion

The activity concentration obtained in the phophogypsum samples are presented in the Table 1 and 2. Samples were analyzed in triplicate.

Table 1. Average concentrations of ^{226}Ra, ^{232}Th and ^{40}K (Bq kg^{-1}) from phosphogypsum bricks.

	Concentrations(Bq kg^{-1})		
Samples	^{226}Ra	^{232}Th	^{40}K
Ultrafertil	388 ± 4	273 ± 5	< 22
Fosfertil	307 ± 2	175 ± 4	< 22
Bunge	30 ± 6	37 ± 5	< 22

Table 2. Average concentrations of ^{226}Ra, ^{232}Th and ^{40}K (Bq kg^{-1}) from phosphogypsum plates.

	Concentrations(Bq kg^{-1})		
Samples	^{226}Ra	^{232}Th	^{40}K
Ultrafertil	392 ± 10	253 ± 3	< 81
Fosfertil	294 ± 3	151 ± 6	< 56
Bunge	16 ± 1	26 ± 3	< 39

The concentrations obtained in this work are in good agreement with values reported in literature for Brazilian phosphogypsum [3]. Ultrafertil and Fosfertil industries presented higher values for the activity concentration; the results obtained for phosphogypsum from Bunge industry are lower and of the same order of magnitude of the total average radionuclides concentration in soil from UNSCEAR [1].

Table 3 presents results of radium equivalent activities and external and internal hazard indices.

Table 3. Radium equivalent activities ($C_{Ra,eq}$) and external and internal hazard index.

Samples (bricks/plates)	$C_{Ra,eq}$ (Bq kg^{-1})	Hazard indices ext.	Hazard indices int.
bricks (Ultrafertil)	780	2.1	3.2
bricks (Fosfertil)	559	1.5	2.3
bricks (Bunge)	84	0.2	0.3
plates (Ultrafertil)	755	2.0	3.1
plates (Fosfertil)	512	1.4	2.2
plates (Bunge)	55	0.2	0.2

The results of radium equivalent, external and internal hazard indices showed that plates and bricks from Ultrafertil and Fosfertil present values above the recommended limits, suggesting the application of a more realistic model for the evaluation of the exposure in dwelling. Maduar et al. [14], using an experimental house with walls and roof made with phosphogypsum of different origins evaluated the dose conversion factors for the external exposure. The results obtained in this paper showed that the annual increment in the effective dose to an inhabitant of the house is below the 1 mSv limit for this specific scenario.

Table 4 presents the results of radon exhalation rate from bricks and plates made of phosphogypsum, these results are in accordance with literature values for phosphogypsum blocks [20], and are of the same order of magnitude of ordinary building materials, such as sand and concrete [21-22]. The radon exhalation rate was also measured in the Brazilian phosphogypsum stacks from Fosfertil and Ultrafertil giving results varying from 341 to 562 Bq m^{-2} h^{-1}, respectively [15]. The results obtained in the phosphogypsum stacks were two orders of magnitude higher than those from plates and bricks, giving evidence that the porosity, density and gas diffusion coefficient in the material play an important role in the radon exhalation.

Table 4. Radon exhalation rate from bricks and plates made of phosphogypsum (Bq m^{-2} h^{-1}).

Samples	Bricks (Bq m^{-2} h^{-1})	Plates (Bq m^{-2} h^{-1})
Ultrafertil	5.67	4.30
Fosfertil	3.78	3.21
Bunge	0.41	0.16

4. Conclusion

The results of radium equivalent, external and internal hazard indices for phosphogypsum form Ultrafertil and Fosfertil were above the recommended levels. Therefore, further studies using more realistic models are necessary for the safe application of phosphogypsum as building material.

The ^{222}Rn exhalation rates from phosphogypsum plates and bricks are of the same order of magnitude of ordinary building materials, such as sand and concrete, therefore its use will note imply in any additional risk for dwellings due to radon inhalation.

The results obtained in this study will contribute for the establishment of guidelines by the Brazilian regulatory agency for the safe use of phosphogypsum as building material.

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