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APPLICATION OF SEMI-EMPIRICAL MODEL FOR THE EVALUATION OF RADIUM ACTIVITY IN PHOSPHOGYPSUM USED AS COMPONENT OF CLINKER

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ABSTRACT

Phosphogypsum is a residue that has been used by the cement industry as a substitute for the natural gypsum, used as a clinker additive during the production of Portland cement. There is a potential increase in this residue use since the large amount of phosphogypsum is generated as outcome of the phosphate fertilizer industries. However, phosphogypsum can be considered a source of radioactive contamination since it has ^{226}Ra in its composition. Depending on the concentration of ^{226}Ra, from the radiological protection point of view, this may cause a problem because this radionuclide and its direct decay product ^{222}Rn along with other decay products, represent the largest fraction of radiation internal dose received by people. In order to evaluate the level of radiological risk that may be associated with the use of phosphogypsum, it is necessary to identify the concentration of ^{226}Ra in building material. The aim of this research is to analyze the samples of phosphogypsum in relation to the concentrations of ^{226}Ra, determined indirectly through ^{222}Rn activity measurements. This measurement process has the advantage of being fast, convenient and relatively inexpensive when compared to traditional ^{226}Ra concentration in samples measurement methods. Proposed physical-mathematical model was used to establish radium concentration from radon exhalation rate from cement mortar samples. The ^{222}Rn activity measurements were performed with a portable detector with cubic phosphate samples with dimensions of 50x50x50mm^3 allocated in a closed atmosphere of sampling chamber until secular equilibrium was reached. Obtained concentrations of radium activity in studied samples of phosphogypsum and cement mortars were found below the limits recommended by CNEN and international regulation.

1. INTRODUCTION

The human being is exposed to ionizing radiation from several radioactive sources, among which the most outstanding is natural radiation. Exposure to this type of radiation can occur in two ways: externally, from the radiation contained in rocks and soils that constitute the earth's crust as well as building materials obtained from the processing of these, in addition to cosmic radiation; and internally, by inhaling the air and ingestion of water and food contaminated by radioactive elements. The radioactive elements present in the Earth's crust since its formation are called primordial radionuclides. These radionuclides may belong to different radioactive series, of which the most important from the point of view of radiological protection are ^{238}U and ^{232}Th, besides ^{40}K occurring in isolation. Exposure to these radionuclides, as well as to their decay products, can significantly increase external exposure to radiation due to gamma emissions [1].

During the ^{238}U radioactive decay process, through three alpha decays and two beta decays the ^{226}Ra is generated. This radionuclide belongs to the family of alkaline earth metals and is found in the solid phase having a half-life of 1600 years, and when decaying radioactively by emission of an alpha particle generates ^{222}Rn, and together with its decay products represent the largest fraction of the dose of internal radiation received by humans, since these radionuclides are present in different concentrations in rocks, soils, groundwater, air and building materials [2].

^{222}Rn has very specific characteristics: it is odorless, tasteless, colorless and has a half-life of approximately 3.8 days [3]. By means of transport processes, the 222Rn present in soil and rocks diffuses easily into groundwater, air and building materials [4] thus increasing its concentration in indoor environments with poor ventilation. The ^{222}Rn is a radioactive gas that when inhaled decays probabilistically within the lungs by emission of alpha particles. It is observed that 222Rn along with its short half-life children are the main contributors to the effective dose related to lung cancer [5].

The processing of natural resources (rocks and soil from the earth's crust) for the purposes of technological and social development is a practice that exposes humans to different levels of ionizing radiations in different places, especially indoors. This may produce an increase in the radiation dose received since these materials may contain significant amounts of ^{238}U and ^{232}Th in addition to the radionuclides progenies. Because of this, the scientific community has developed standards and procedures that aim to quantify the concentration of natural radionuclides in different materials, so that radiation exposure limits can be stipulated to prevent detrimental to human health [2].

A TENORM material is a residue obtained by the processing of rocks is phosphogypsum. This material is generated during the wet production process of phosphoric acid by the phosphate fertilizer industries [6], in which the apatite rock or phosphorite is chemically attacked with sulfuric acid, generating phosphoric acid as principal product and phosphogypsum as a byproduct [7]. During the chemical attack of the rock occurs the breakdown of the radioactive balance between the radionuclides of the natural series, causing them to be redistributed to the various stages of the reaction according to their physical and chemical properties, affinity, solubility beyond the operational conditions [8] . Thus, uranium, thorium and ^{210}Pb are redistributed preferentially to phosphoric acid, whereas ^{226}Ra, ^{228}Ra and ^{210}Po are redistributed to phosphogypsum that contain also calcium, some trace elements (Cd, As, Pb and Zn) and fluorides [9].

The phosphate fertilizer industries are responsible for most of the phosphogypsum produced worldwide, and for each ton of phosphoric acid produced, approximately 4.3 tons of phosphogypsum is obtained [10]. In Brazil, the main phosphate fertilizer producing industries are located in state of São Paulo and in state of Minas Gerais. Together, these industries produce approximately 5.5 million tons of phosphogypsum per year [11].

Due to the large volume produced of this residue, its storage is done most of the time outdoors in areas near the producing industry. However, such storage may cause undesirable effects on the environment and to the population living near such locations. Among the major problems are atmospheric contamination by fluorides, pollution of groundwater by labile anions, acidity, trace elements, besides radon emanation, radioactive dust inhalation and direct exposure to gamma radiation [12]. Studies developed worldwide show that of all phosphogypsum produced, 58% are stored, 28% are discarded in sedimentation ponds and only 14% are reprocessed [13].

Thus, the reuse of phosphogypsum is of fundamental importance, since this residue presents potential of use in several areas, and its application would result in a reduction of the economic-environmental impacts generated by its inadequate disposition [6]. In Brazil, of all phosphogypsum produced by the phosphate fertilizer industries, only 10% is reused, being its main use in cement production, agriculture and civil construction [14]. In cement production, the portion of gypsum added to the clinker can be replaced with a maximum content of 5% of phosphogypsum, since both have similar physical and chemical properties [15].

One of the ways of measuring the concentration of ^{226}Ra in building materials is from the direct measurement of ^{222}Rn concentration [16]. A non-destructive technique is used, where the measurement of the radon concentration can be made by a portable detector AlphaGUARD of high sensitivity and fast linear response, that besides providing the concentration of this radionuclide presents information about the temperature, humidity and pressure [17]. From the concentration of ^{222}Rn obtained in a confined atmosphere, a mathematical model is applied that allows to infer the concentration of ^{226}Ra in the sample. Among the models available in the literature, we can cite the one developed by Ferry et al., in 2002 [18] and by Jang et al., In 2005 [19]

The present work suggests that the phosphogypsum is reused as a substitute for natural gypsum used with clinker additive during Portland cement production. However, for such an application to be possible from the economic-environmental and radiological point of view, it is necessary to carry out measurements of the concentration of ^{226}Ra and its decay products present in phosphogypsum, since such radionuclides contribute to the increase in the dose of internal radiation received human beings. The measurement of the ^{226}Ra concentration in the phosphogypsum uin this work was made from the semi-empirical physical-mathematical model developed which takes into account the concentration of ^{222}Rn in test specimens constituted of phosphogypsum disposed in confined atmosphere.

2. MATERIALS AND METHODS

2.1 Semi-empirical model

The semi-empirical model used in the present work to determine the activity concentration of element 226Ra from measurements of 222Rn gas concentration in test samples made of 50/50 gypsum / phosphogypsum was developed in the UTFPR Laboratory of Applied Nuclear Physics (LFNA). This model is based on the Fick diffusion law (Eq. 1), which in this particular case suggests that the main transport mechanism of radon gas in solid media is diffusion.

In building materials such as concrete, brick, cement and gypsum there are small amounts of ^{226}Ra as well as ^{222}Rn. Thus, three terms were added to Fick's law. The first called emanation coefficient (ω) takes into account the rate of radon production in the material due to the presence of the radium. The second term is related to the negative of the current density divergence ($\nabla \cdot j$) and the third term is related to the negative of the radon activity density (λ_n)

[18]. Equation (2) shows how Fick's law remained after the aforementioned terms were added to it.

$$\vec{J} = -D\nabla_C \quad (1)$$

$$\frac{\partial_n}{\partial_t} = \omega - \vec{\nabla} \cdot \vec{J} - \lambda n \quad (2)$$

As the radon concentration is measured with the sample disposed in a closed environment, two conditions were considered: (1) the diffusion coefficient (D) in the solid is much lower than in the external atmosphere, DI << DE; (2) that the sample is saturated with ^{222}Rn and the atmosphere is free of that radionuclide, so we have that the number of atoms in the system is equal to the equilibrium value in the solid, N0 = N1 (∞) . These conditions are met if the samples are left in a hermetically sealed flask for 40 days so that the elements belonging to the same decay series present in the material reach the secular equilibrium, and thereafter the samples are transferred to a new vial so that the initial concentration of radon in the environment is zero but that the sample is saturated with this radionuclide.

After the application of boundary conditions, experimental adjustments and application of the two previous conditions, we reached the physical-mathematical model used in this work (Eq. 3), which makes it possible to calculate the mean concentration of ^{222}Rn in a confined atmosphere as well as to infer the specific activity concentration of ^{226}Ra from the measurement of the radon concentration in the material.

$$\bar{n}_B(t) = \beta^2 \frac{\omega}{\lambda}(1 - \gamma\beta^2 e^{-\lambda t}) - \bar{a}_1 e^{-\lambda_1 t} - \bar{a}_2 e^{-\lambda_2 t} \quad (3)$$

In this equation:

$\beta = \sqrt{\frac{D_I}{D_E}}$, where D_I and D_E are the diffusion coefficients in the solid and in the external atmosphere;

$\gamma = \frac{V_E}{V_I}$, com V_E and V_I being the volumes of the external atmosphere and the solid, respectively;

$\bar{a} = \frac{A_k}{V_E}$, where A_k depends on the boundary conditions;

ω is the emanation coefficient of ^{222}Rn in the solid;

λ is the decay constant of ^{222}Rn;

t is the time, in hours, that the radon concentration was measured by the AlphaGUARD equipment;

$\lambda_1 = D_I k_1^2 + \lambda$ e $\lambda_2 = D_I k_2^2 + \lambda$, onde k_1 e k_2 represent the first and second roots of the transcendental equation (4):

$$\beta \sin(\kappa\beta L_E)\cos(\kappa L_I) + \sin(\kappa L_I)\cos(\kappa\beta L_E) = 0 \tag{4}$$

Equation (4) is used to determine the values of κ, which in turn are used to calculate the parameters a¯of equation 5. The values of κ depend on the initial and boundary conditions. The terms L_E and L_I are the lengths of the outer atmosphere and the solid, respectively.

2.2 Samples preparation

The gypsum/phosphogypsum samples were prepared as following. First, the gypsum and phosphogypsum obtained in powder form were sieved in a 1.2 mm aperture sieve to separate larger particles and impurities. After this, the materials were dried for drying in at 150 °C, where they remained for 24 hours, in previous research [20].

Subsequently the gypsum was mixed with phosphogypsum in the ratio of 50/50. After that, this mixture was sprinkled on water for 1 minute until a homogeneous paste was obtained, which was then taken to six cubic molds with dimensions of 50 x 50 x 50 mm (Fig 1) and coated with mold release wax where they remained for 24 hours. After the respective time interval, the samples were removed from the molds and placed in a greenhouse at low temperature until complete drying. Figure 2 shows the samples ready for the ^{222}Rn exhalation assay.

Figure 1 – Samples of gypsum/phosphogypsyum sealed and one face filtered

2.3 Measurements of ^{222}Rn activity with AlphaGUARD Detector

The measurement of the exhalation rate of ^{222}Rn in the gypsum/phosphogypsum samples was performed by the AlphaGUARD portable detector produced by Saphymo GmbH. This detector has as main characteristics the high sensitivity and fast linear response, operating in the range of 2–2,000,000 Bq/m^3). In addition to measuring radon gas concentration, this equipment provides temperature, pressure and humidity measurements [17].

The measurements were carried out with three samoes arranged in a glass container with a volume of approximately 3.3 L, which were hermetically sealed for 40 days in order to allow radionuclides ^{226}Ra and ^{222}Rn to reach secular equilibrium. To satisfy the conditions mentioned in topic 2.1, the samples were removed from the container where they remained for 40 days and immediately placed in another empty container equivalent to the first.

After this, the AlphaGUARD was switched on in the 10 min / flow mode, and waited until the equipment indicated the start of the measurement. After that, the AlphaPUMP air pump in the 0.5 L/min mode was connected to the detector by a set of tubes, and this made the air circulate inside the atmosphere. Each measurement is performed for 12 days. Figure 2 shows the system used to acquire the data.

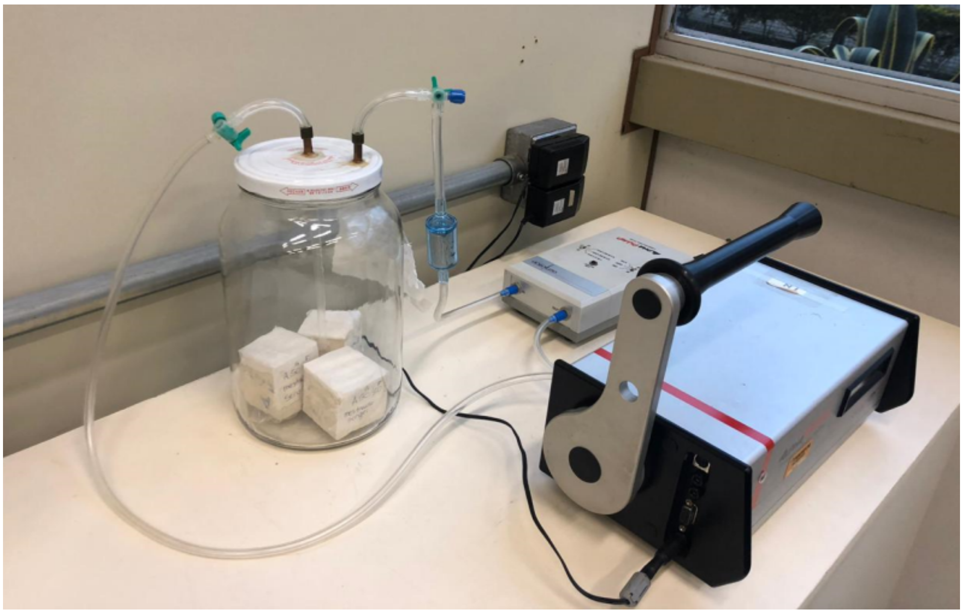

Figure 2 – System used to measure radon concentration

The model used for the measurements of radon gas exhaled by the samples was called *one-dimensional long duration model*. In this model only the surface of the sample by which the gas is desired to be exhaled is covered with filter paper to prevent dirt particles from coming out of the material from entering the ionization chamber of the equipment interfering with the measurements, the other surfaces are sealed and wrapped with film paper.

In this work, five of the faces of the cubic specimens were sealed with film paper and only the top face was covered with filter paper, the gas being exhaled by this face. The concentration of activity measured by the detector, in Bq/m^3, is given by the product of the ^{222}Rn decay constant and its mean concentration in a closed atmosphere. The half-life of the ^{222}Rn used was 3.8 days, which when converted to decay constant, resulted in a value of approximately $2,10 \times 10^{-6}$ s^{-1}.

3. RESULTS AND DISCUSSION

Based on the ^{222}Rn concentration data obtained by the AlphaGUARD detector, it was possible to obtain the activity concentration of element ^{226}Ra by adjusting the physical-mathematical model (eq.3) used in the present work. Figure 3 shows the curve obtained from the semi-empirical model adjustment.

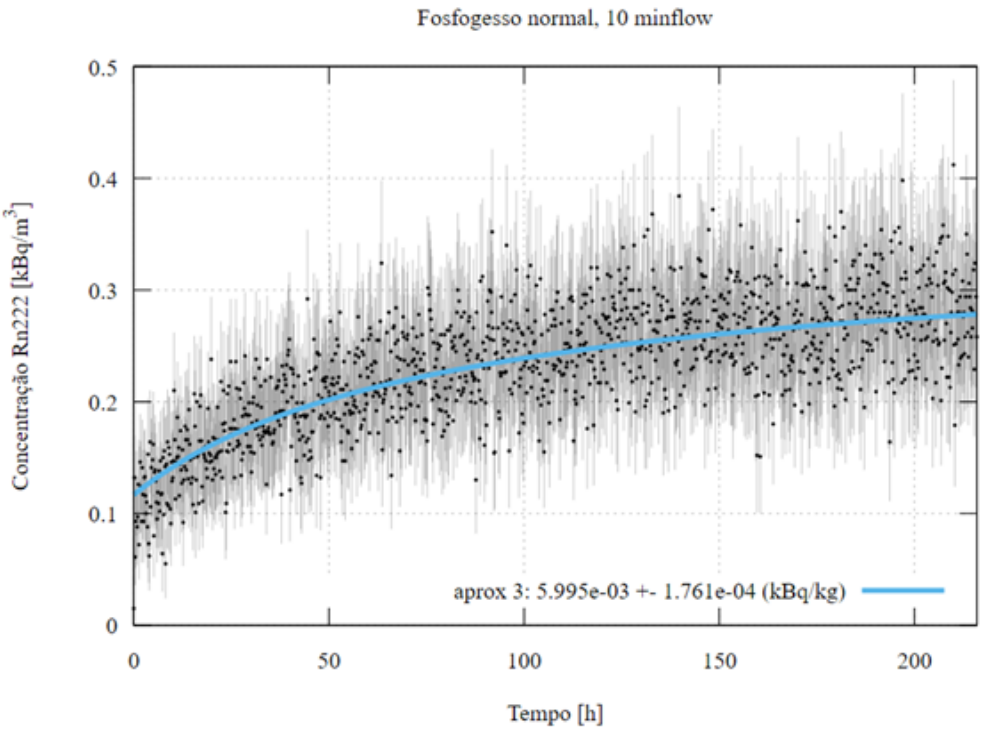

Figure 3 - Curve obtained from the semi-empirical model adjustment

It can be seen in Figure 3, a displacement of the curve from the concentration axis. This suggests that the ionization chamber of the AlphaGUARD detector had some concentration of radon (background). However, at the level of the curve obtained, this initial value different from zero, due to the time of collection of measurements (288 hours) can be considered negligible.

In the case of adjustments to higher concentration data from contaminated concretes and/or mortars, or phosphogypsum containing radio at higher concentrations, the background background values of the measurement system are unimpressive compared to the actual concentrations of the materials. In the case of measurements where the concentration is lower, as in the case of the phosphogypsum under analysis, there is the displacement mentioned.

The value obtained for the concentration of ^{226}Ra activity in the phosphogypsum analyzed was compared with the value obtained by gamma ray spectrometry for the same material, performed at the Nuclear and Energy Research Institute (IPEN). This comparison aims to validate the semi-empirical physical-mathematical model. The results obtained for the concentration of the radionuclides radium and radon, from the use of the model, are in Table 1.

Table 1 – Values of activity concentrations of radionuclides ^{226}Ra and ^{222}Rn obtained by the physical-mathematical model

Radionuclide	Activity Concentration (Bq/kg)	Material (*ratio* 50/50)
^{226}Ra	6.0 ± 0.18	Gypsum/Phosphogypsum
^{222}Rn	273.2 ± 1.91	Gypsum/Phosphogypsum

Table 2 shows the activity concentration values of radionuclides ^{226}Ra, ^{228}Ra, ^{210}Pb, ^{40}K and ^{228}Th obtained by gamma-ray spectrometry.

Table 2 – Values of activity concentrations of radionuclides ^{226}Ra, ^{228}Ra, ^{210}Pb, ^{40}K and ^{228}Th obtained by gamma-ray spectrometry

Radionuclide	Activity Concentration (Bq/kg)	Material (*ratio* 50/50)
^{226}Ra	8.0 ± 2.0	Gypsum/Phosphogypsum
^{228}Ra	14.0 ± 1.0	Gypsum/Phosphogypsum
^{210}Pb	18.0 ± 3.0	Gypsum/Phosphogypsum
^{40}K	8.0 ± 6.0	Gypsum/Phosphogypsum
^{228}Th	13.0 ± 2,0	Gypsum/Phosphogypsum

It can be observed that the value of the concentration of ^{226}Ra activity obtained by the model used in the present work (Table 1) is very close to the value obtained by gamma ray spectrometry (Table 2). This result demonstrates that the model can be an alternative to the application of the gamma ray spectrometry technique with regard to the determination of the activity concentration of this radionuclide in samples of construction materials, since their application depends only on the measurement of the concentration of the ^{222}Rn, which is made by an AlphaGUARD detector, that is, it is a low cost technique, compared to the spectrometry.

4. CONCLUSION

The use of the semi-empirical physic-mathematical model (Eq. 3) to determine the activity concentration of ^{226}Ra element from indirect measurements of ^{222}Rn gas in samples of gypsum/phosphogypsum mortar is a viable alternative, mainly from the point of view when compared to the use of the gamma ray spectrometry technique, since its application depends only on measurements of the radon gas made by the AlphaGUARD detector in a closed atmosphere. The data of tables (1) and (2) show that the values found for the concentration of ^{226}Ra activity by the different techniques are very close, validating the use of the model in question. With regard to elements ^{226}Ra and ^{228}Ra, CNEN stipulates a limit value of 1000 Bq / kg for the activity concentration of these radionuclides present in phosphogypsum used in agriculture and cement industry, ie. the value found for gypsum/phosphogypsum mortar analyzed in the present work, is well below the limit value stipulated by CNEN, and it can be applied in the cement industry without restriction.

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