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Phosphogypsum recycling in the building materials industry: assessment of the radon exhalation rate

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ABSTRACT

Phosphogypsum can be classified as a Naturally Occurring Radioactive Material (NORM) residue of the phosphate fertilizer industry. One of the main environmental concerns of its use as building material is the radon exhalation. The aim of this study is to measure the radon exhalation rate from plates and bricks manufactured with phosphogypsum from three installations of the main Brazilian producer, Vale Fertilizantes, in order to evaluate the additional health risk to dwellers. A simple and reliable accumulator method involving a PVC pipe sealed with a PVC pipe cover commercially available with CR-39 radon detector into a diffusion chamber was used for measuring radon exhalation rate from phosphogypsum made plates and bricks. The radon exhalation rate from plates varied from 0.19 ± 0.06 Bq m^{-2} h^{-1}, for phosphogypsum from Bunge Fertilizers, from 1.3 ± 0.3 Bq m^{-2} h^{-1}, for phosphogypsum from Ultrafertil. As for the bricks, the results ranged from 0.11 ± 0.01 Bq m^{-2} h^{-1}, for phosphogypsum from Bunge Fertilizers, to 1.2 ± 0.3 Bq m^{-2} h^{-1}, for phosphogypsum from Ultrafertil. The results obtained in this study for the radon exhalation rate from phosphogypsum plates and bricks are of the same order of magnitude than those from ordinary building materials. So, it can be concluded that the recycling of phosphogypsum as building material is a safe practice, since no additional health risk is expected from the radiological point of view.

1. Introduction

In the last years, there has been an increased interest in measuring radionuclides concentration in building materials and radon levels in the air at homes, due to their potential risk to human health (Campos and Pecequilo, 2003; Cazula et al., 2015; EC, 1999, Todorović et al., 2014; Turhan et al., 2008; Kovler, 2009). Exposure to radon accounts for more than 50% of the annual effective dose from natural radioactivity (UNSCEAR, 2000).

Radon in a house comes mainly from the soil adjacent to the foundation. However, radon exhalation from building materials is another potential source of the gas in indoor environment.

Building materials are an important radon source in houses since they can contain small amounts of natural radionuclides such as ^{226}Ra, ^{232}Th and ^{40}K. The radionuclides content is usually low, but some materials, like phosphogypsum, may contain higher concentrations depending on the origin of the raw material used. The presence of radionuclides puts restrictions on the use of phosphogypsum in building materials and in soil amendments. The Brazilian regulatory body ruled that phosphogypsum would only be permitted for use in agriculture or in the cement industry if the concentration of ^{226}Ra and ^{228}Ra does not exceed 1 Bq g^{-1} (CNEN, 2014). Recently, a working group was established at the national regulatory level in Brazil, aiming to define a policy for using phosphogypsum as construction material.

Phosphogypsum is a waste of the phosphate fertilizer industry. It is formed by the chemical attack of the phosphate rock with sulphuric acid to produce phosphoric acid. This waste is generally stored in piles near the fertilizer factory. Phosphogypsum can be classified as a NORM residue, *Naturally Occurring Radioactive Material,* which means that its reuse may pose risks to human and environment from the radiological protection point of view (El Afifi et al., 2007; IAEA, 2013a). The radiological impact assessment of NORM residues on the environment should comprise the release of radon isotopes into the atmosphere (IAEA, 2013b).

The residues containing NORM altered by human activities has received considerable amount of global attention over the last decades. The main concern is the large amount of this residue and consequent long-term risk due to the presence of radionuclides

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with long half-lives and high radiotoxicity. According to TECDOC 1712 “Management of NORM Residues” from International Atomic Energy Agency (IAEA, 2013c), it is necessary changing attitudes towards NORM residues. This document emphasizes that “… *there is an overall trend worldwide towards greater recycling of NORM residues and their use as by-products. This is being driven by sustainability issues such as concerns over the depletion of non-renewable resources, by more stringent environmental protection legislation, by a growing recognition that the amounts of NORM disposed of as waste need to be minimized in order to make their disposal manageable, and sometimes simply by economic considerations, some of which become evident only when the true costs and liabilities of NORM residue disposal as waste are taken into account. Some countries are now making specific provision in their regulatory systems for NORM residue recycling and use”*. Therefore, there is an overall trend in recycling phosphogypsum, provided that such practice will not cause additional radiological health risk to the public.

Phosphogypsum has been used in cement industry, as sub-base of roads, as building material and as soil amendment. Phosphogypsum has become an item of commercial interest in many countries, with a well-established market value in agriculture and construction. However, the commercial use of phosphogypsum has been restricted because of concerns about its radioactivity content. Relatively high radioactivity, particularly ^{226}Ra activity concentration (Dueñas et al., 2007, Mazzilli et al., 2000), among other impurities, can prevent its reuse for several purposes.

The worldwide phosphogypsum production is estimated to be at 160 million t (IAEA, 2013a) per year and only 14% is recycled and used as building material (Máduar et al., 2011). Production is increasing worldwide and could reach up to 250 million t within the next twenty years. Approximately 3 billion t of phosphogypsum are stored in piles of various sizes in well over 50 countries (IAEA, 2013a).

The Brazilian annual production of phosphogypsum reaches 12 million tons (DNPM, 2014), and Brazil, like other countries that produce this residue, is trying to find safe solutions for its reuse. One possible application of phosphogypsum is in the manufacturing of building materials. However, an evaluation of its radiological impact is required, mainly due to the radionuclides content and radon exhalation rate. Several studies were published concerning the radiological impact of using Brazilian phosphogypsum as building material, comprising the measurement of the radionuclides content, as well as the internal and external exposure of dwellers (Campos et al., 2011; Máduar et al., 2011, Mazzilli and Saueia, 1999; Nisti et al., 2013; Rabi and Silva, 2006). Since most of the Brazilian phosphogypsum contains traces amounts of radium isotopes, a main concern to the dwellers is the inhalation of radon and consequent internal exposure. The radon exhalation rate of 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 coefficient, gas diffusion coefficient in the material, porosity and density of the material (Dueñas et al., 2007; Sharma and Virk, 2001).

The aim of this study is to determine experimentally the radon exhalation rate from bricks and plates made of phosphogypsum, in order to evaluate if these building materials pose no additional health risk to dwellers due to radon exhalation. A practical approach to measure radon exhalation rate directly from the surface of the material is to allow the radon build up in a container, known as accumulator, over time (Chen et al., 2010; Kotrappa and Stieff, 2009; Sharma et al., 2003; Shweikani and Raja, 2009) and measure the radon content by passive method with solid state nuclear track detectors (SSNTD). The phosphogypsum bricks and plates evaluated in this study were manufactured by UCOS (humidification, compaction and drying) method (Novogesso® Technology) (Kanno et al., 2007), with phosphogypsum provided by Vale Fertilizers, the main Brazilian phosphate fertilizer producer.

2. Materials and methods

Several methods to measure radon exhalation rate from building materials make use of accumulators associated with alpha particle detectors, such as, continuous gas monitor, scintillation cell, ionization chamber and solid state nuclear track detector (Kobeissi et al., 2013; Lettner and Steinhäusler, 1988; Righi and Bruzzi, 2006; Tuccimei et al., 2006). In this study, a simple and reliable accumulator method with CR-39 into diffusion chambers was used for measuring radon exhalation rate from phosphogypsum building materials.

Eighteen samples of plates and fifteen samples of bricks manufactured with phosphogypsum provided by Vale Fertilizantes were analyzed for the ^{222}Rn exhalation rate. The phosphogypsum producers are namely Ultrafertil located in Cubatão, Fosfertil located in Uberaba and Bunge Fertilizers located in Cajati. Five samples of brick manufactured with natural gypsum were also analyzed.

A Polyvinyl chloride (PVC) pipe sealed with a PVC pipe cover commercially available of know dimensions (7.2 cm diameter and 30 cm height) was used as the accumulator. As reported by Tuccimei et al. (2006), PVC can be considered a radon-tight material, unless exposed to high levels of gamma radiation that can affect its radon permeability. The accumulator was placed on the phosphogypsum bricks and plates and the contact between the accumulator and samples was sealed with silicone adhesive. A CR-39 in a plastic diffusion chamber (passive radon detector) was placed inside the accumulator at a distance of 25 cm from the surface of the sample, in order to count only the ^{222}Rn contribution and to avoid the role of ^{220}Rn from the surface of phosphogypsum building materials samples (Faheem and Matiullah, 2008; Shafi-ur-Rehman et al., 2006). This passive radon detector assures the discrimination of radon decay products by allowing only the gas to enter the diffusion chamber (Bartlett et al., 1988). The exhalation rate was determined through the radon concentration at the accumulator.

At the accumulator closed system (Faheem and Matiullah, 2008; Rahama et al., 2007), the passive radon detector is exposed to variable concentrations, starting from zero to equilibrium concentration. So, in order to calculate the radon concentration at the accumulator, it is necessary to determine the effective exposure time. The effective exposure time of the passive detectors to radon was calculated through the following equation (Shweikani and Raja, 2009):

$$t_{eff} = t - \frac{1}{\lambda}\left(1 - e^{-\lambda \cdot t}\right) \qquad (1)$$

where: t is the real exposure time and λ is ^{222}Rn decay constant.

The detectors were exposed to radon for 30 days. After exposure, CR-39 detectors were etched in a KOH (30% mass weight) solution at 80 °C for 5.5 h in a constant temperature bath (Máduar et al., 2011; Manocchi et al., 2014). After etching, CR-39 detectors were washed, dried and counted under a Carl Zeiss microscope for track density measurements. The background was 12 ± 2 tracks per cm^2. The track density was related to radon concentration in the environment, by using a calibration factor of 2.14 ± 0.17 tracks cm^{-2} per kBq m^{-3} h, obtained with Pylon model RN-150 calibrated radon gas source. Radon concentration in the accumulator was calculated through the following equation (Shweikani and Raja, 2009):