RADIOLOGICAL IMPLICATIONS

of using phosphogypsum as building material

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INTRODUCTION

Introduction

- The necessity to implement effective management of wastes and residues, including those containing NORM, was presented in the meeting Agenda 21 held in Rio de Janeiro 1992.

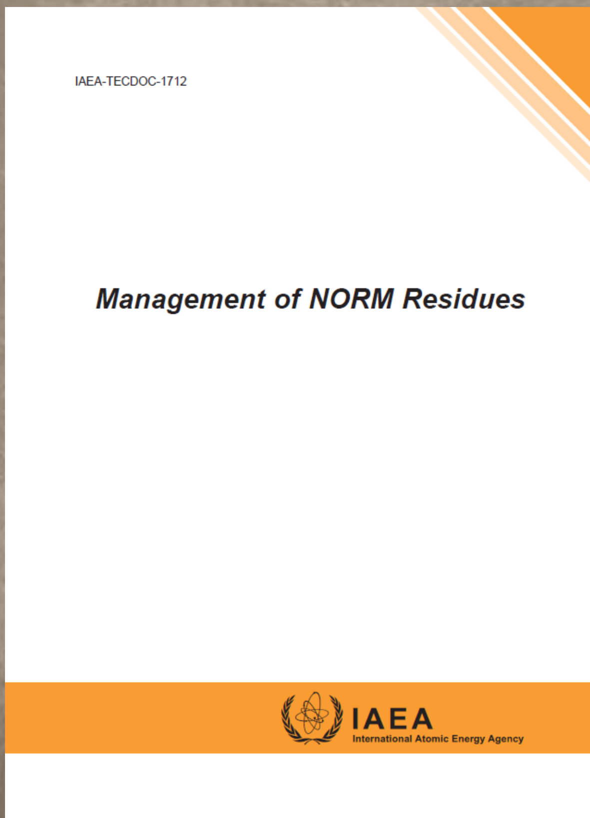
- United Nations Conference on Environment and Development (UNCED) emphasized the necessity to: **reduce the amount of all types of waste being generated and manage all waste in a manner that protects human health and the environment**.

- Hence, an important step for industry and regulatory bodies in a country is to understand when and where NORM can occur within a given process and also to identify the locations where concentrations of NORM can be greatest within a given process.

- Determining at what concentration for a given exposure situation NORM becomes a potential radiological concern is a high priority in each country.

NORM REGULATION

Management of NORM residue


IAEA-TECDOC-1712

Management of NORM Residues

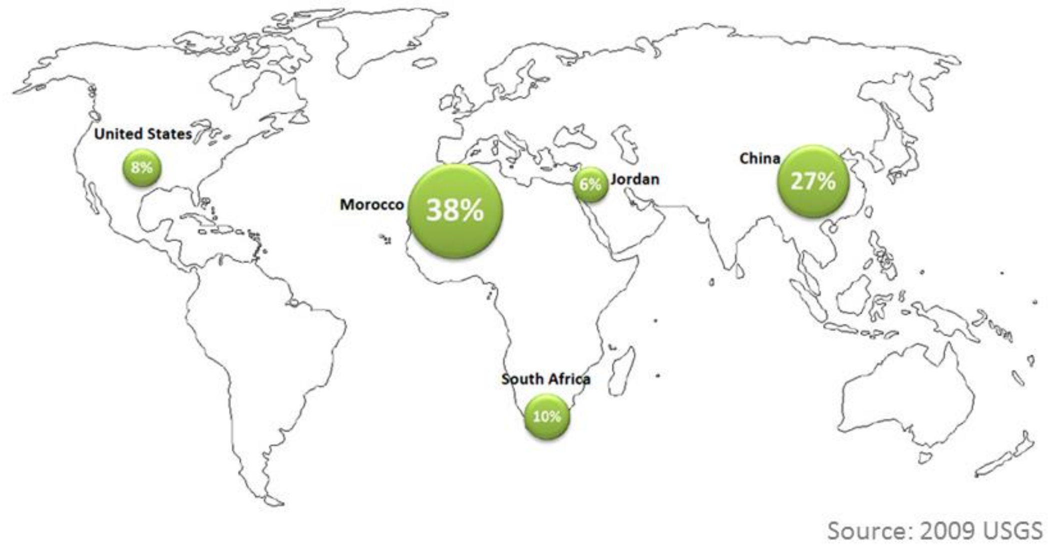
IAEA International Atomic Energy Agency

The general clearance criteria is achieved for a material containing radionuclides of natural origin, when the activity concentration of radionuclides of the U and Th series is below 1 Bq g^{-1} and the ^{40}K activity concentration is below 10 Bq g^{-1}.

"(...) 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 (...)"

Therefore, the NORM industries present a potential environmental and occupational radiological risk. The main concern is the presence of high concentration of radioactive material in the **residue**, which is stored in the vicinity of the installation.

PHOSPHATE INDUSTRY AND PHOSPHOGYPSUM



Global distribution of phosphate deposits

- Phosphates fertilizers are primarily derived from phosphate rock mined as naturally occurring ores.

- The principal constituent of the phosphate rock is the mineral apatite. The typical P_2O_5 concentration of the rock is of the order of 15-30%. Sedimentary, igneous, weathering and biological processes form the phosphate rock.

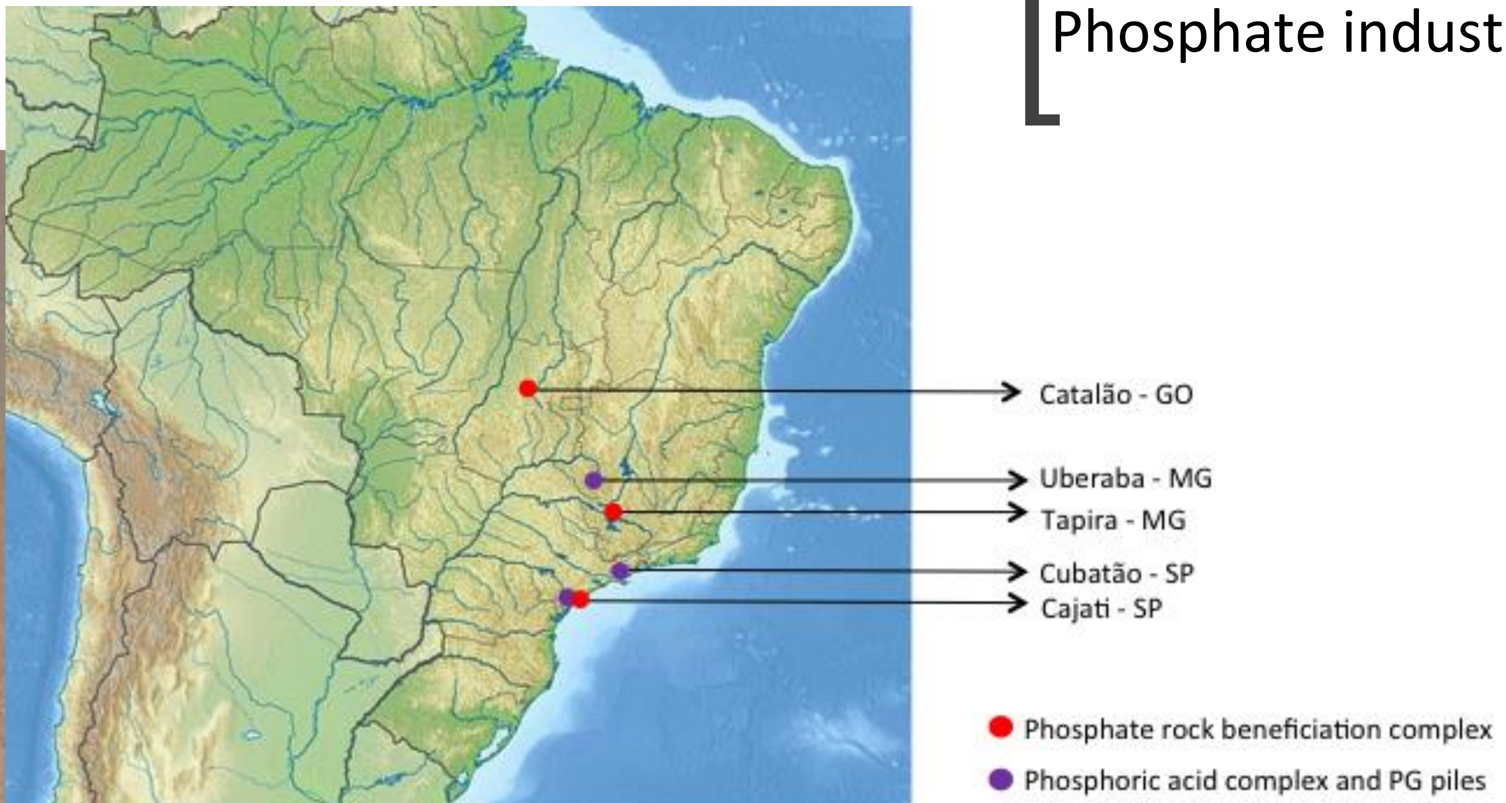
- Approximately 30 countries produce phosphate rock for use in domestic market or for export. Brazil is the sixth country supplying phosphate rock in the international ranking.

Brazilian production of P_2O_5

- According to DNPM, the P_2O_5 Brazilian production in 2013 was 6.7 million tones, ranking as the main phosphate producer of South America.

- The main Brazilian producers of phosphate fertilizers are Vale Fertilizantes and Anglo American/Copebras.

Phosphate industry in Brazil



The phosphate rock is extracted mainly in Tapira-MG, Catalão-GO and Cajati-SP, with P_2O_5 content of the order of 12%. After the extraction, the mineral is beneficiated to 35% of P_2O_5 content and then used for the production of phosphoric acid in other locations.

Radionuclides flows following sulphuric acid acidulation

- In the Brazilian industries, the phosphoric acid is produced by the attack of apatite with sulphuric acid, forming calcium sulfate precipitate ($CaSO_4nH_2O$), known as phosphogypsum, which is considered a residue due to its content of impurities and is stored in stacks.

- The conversion of apatite takes place according to the following general equation:

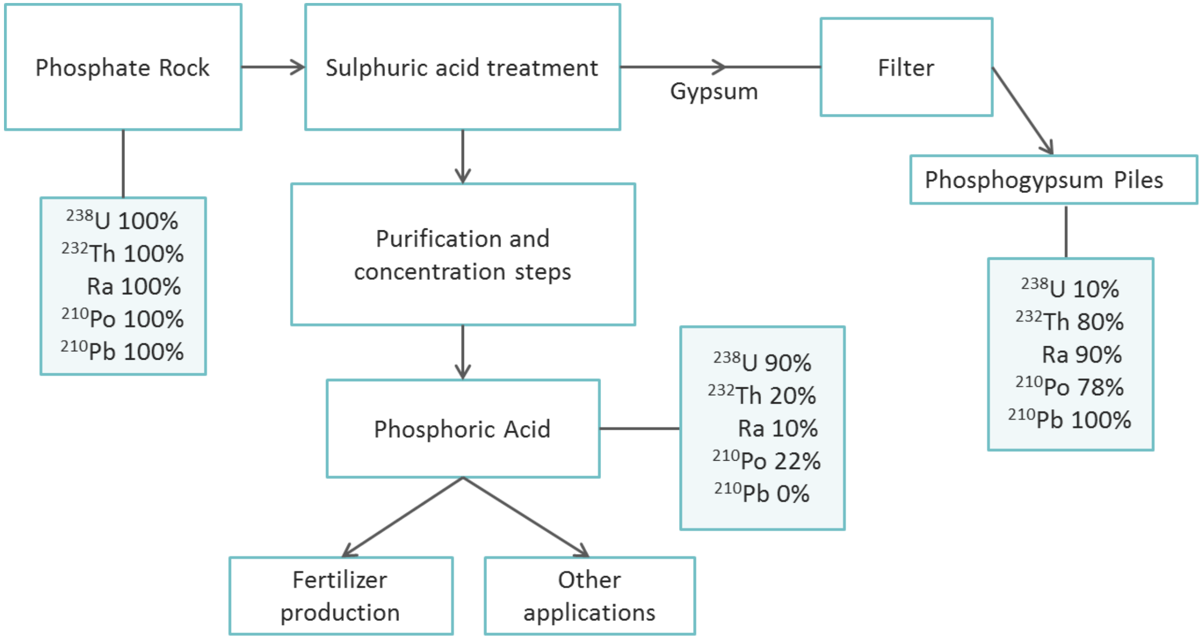
$$Ca_{10}F_2(PO_4)_6 + 10H_2SO_4 + 10nH_2O \rightarrow 10CaSO_4nH_2O + 6H_3PO_4 + 2HF$$

- In the phosphate rock, the radionuclides of the U and Th series are in equilibrium.

- During the chemical process, this equilibrium is disrupted and the radionuclides migrate in the products, by-products and residue according their chemical properties and solubility.

- In terms of rounded figures, the production of 1 ton of phosphate results in the generation of 4-5 ton of phosphogypsum.

Distribution of radionuclides in the sulphuric acid extraction process

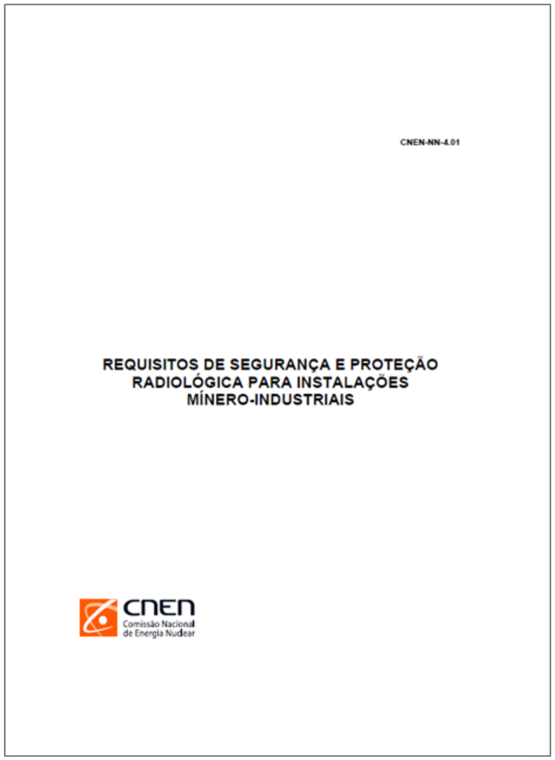


Radium isotopes, Pb-210, Po-210 and thorium isotopes fractionate preferentially to the phosphogypsum, where percentages of 90% (radium isotopes), 100% (Pb-210), 78% (Po-210) and 80% (thorium isotopes) are found. The uranium isotopes are predominantly incorporated in phosphoric acid.

Phosphogypsum activity concentration (Bq kg^{-1})

	ANGLO AMERICAN - CUBATÃO	VALE FERTILIZANTES - UBERABA	VALE FERTILIZANTES - CUBATÃO
	Range	Range	Range
U-238	42 - 53	50 - 23	40 - 58
Ra-226	550 - 940	122 - 236	280 - 434
Pb-210	834 - 1163	136 - 228	316 - 378
Th-232	189 - 257	60 - 103	172 - 243
Ra-228	210 - 273	124 - 179	191 - 247

Brazilian regulation concerning NORM industries and NORM residues

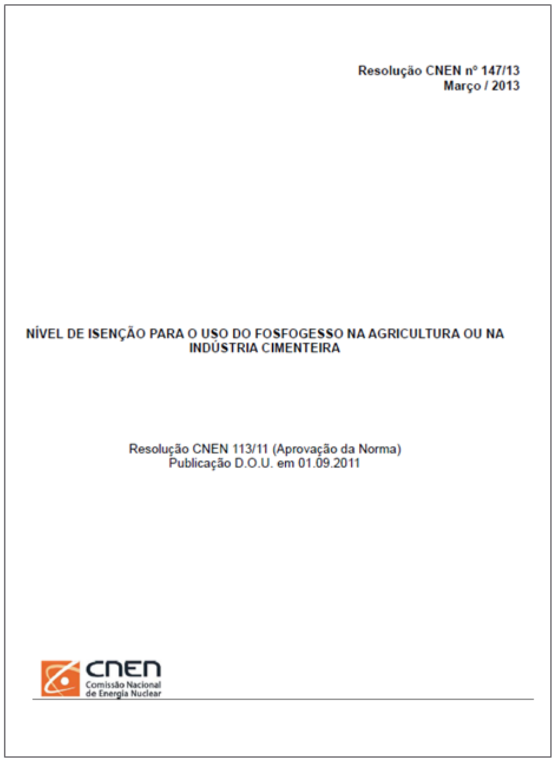

CNEN-NN-4.01

REQUISITOS DE SEGURANÇA E PROTEÇÃO RADIOLÓGICA PARA INSTALAÇÕES MÍNERO-INDUSTRIAIS

CNEN
Comissão Nacional de Energia Nuclear

In Brazil the regulatory agency (Comissão Nacional de Energia Nuclear – CNEN) published a guideline concerning mining and milling of natural occurring radioactive material, which may generate enhanced concentrations of radionuclides, under the radiological protection point of view: Requisitos de Segurança e Proteção Radiológica para Instalações Mínero-industriais CNEN-NN-4.01.

Brazilian regulation concerning NORM industries and NORM residues



Resolução CNEN nº 147/13
Março / 2013

NÍVEL DE ISENÇÃO PARA O USO DO FOSFOGESSO NA AGRICULTURA OU NA INDÚSTRIA CIMENTEIRA

Resolução CNEN 113/11 (Aprovação da Norma)
Publicação D.O.U. em 01.09.2011

CNEN
Comissão Nacional de Energia Nuclear

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, Resolução 147, 2013).

Brazilian regulation concerning NORM industries and NORM residues


Resolução CNEN nº 171/14
Abril / 2014

NÍVEL DE ISENÇÃO PARA O USO DO FOSFOGESSO NA CONSTRUÇÃO CIVIL

Resolução CNEN 171/14
Publicação: DOU 07.05.2014

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Comissão Nacional de Energia Nuclear

Ministério da Ciência, Tecnologia e Inovação

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A few years ago, a working group was established at the national regulatory level in Brazil, aiming to define a policy for using phosphogypsum as construction material. The adopted approach was to limit the concentration of phosphogypsum to be mixed with natural gypsum, based on ^{226}Ra and ^{228}Ra concentrations found in phosphogypsum (CNEN, Resolução 171, 2014).

* THIS GUIDELINE WAS CANCELLED TWO YEARS AFTER ITS IMPLEMENTATION

Phosphogypsum use as building material

- Only a relatively small portion of the worldwide phosphogypsum produced (14%) is reprocessed and used as building material.

- However, it contains relatively high amounts of radioactivity originated mainly from the ^{238}U and ^{232}Th decay series, which can cause health hazards in dwellers.

- ^{226}Ra, which decays to ^{222}Rn through an alpha particle emission, is one of the most important radionuclides from the point of view of radiation protection.

- The principal health hazard associated with ^{222}Rn is due to its short-lived alpha emitter's daughter products, which can cause damage to the lungs after chronic exposure.

Phosphogypsum use as building material

THEREFORE, ITS SAFE UTILIZATION REQUIRES AN EVALUATION OF THE RADIOLOGICAL IMPACT IN DWELLERS, WHICH COMPRISES THE EVALUATION OF INTERNAL EXPOSURE DUE TO RADON INHALATION AND EXTERNAL EXPOSURE DUE TO GAMMA RADIATION.

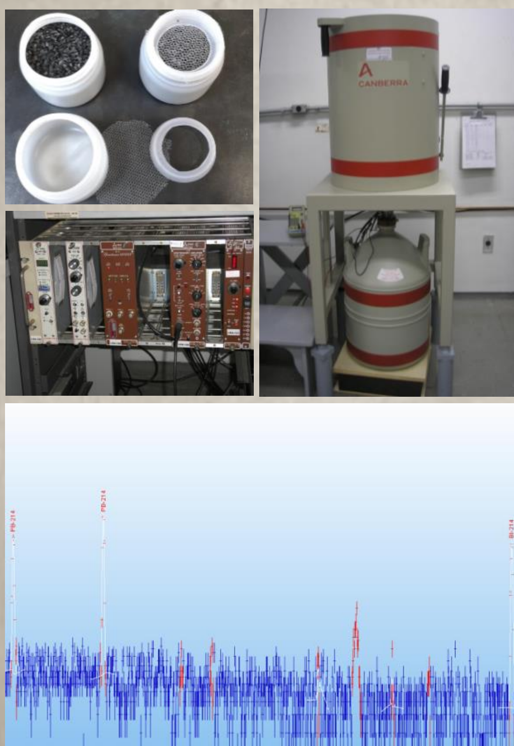
Internal exposure in dwellers due to inhalation of Rn

- The internal exposure indoors depends mainly on the activity concentration of Ra-226 and Ra-228 in the construction material and the radon exhalation rate, which can be determined by using theoretical models or measured experimentally.

- 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.

Internal exposure in dwellers due to inhalation of Rn

Exhalation of radon from phosphogypsum piles obtained experimentally



Activated charcoal collector / HPGe detector and associated electronics / Typical gamma-ray spectrum

- The radon exhalation rate from phosphogypsum piles from phosphate fertilizer industries, was measured experimentally by using the activated charcoal collector method. The ^{222}Rn exhalation rate from phosphogypsum 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; all results were corrected by date of removal of the phosphogypsum collector and its exposure period.

Internal exposure in dwellers due to inhalation of Rn

Exhalation of radon from phosphogypsum piles obtained experimentally

FOSFERTIL , UBERABA-MG

Internal exposure in dwellers due to inhalation of Rn

Exhalation of radon from phosphogypsum piles obtained by a theoretical model

A theoretical model for radon exhalation calculation, suggested by UNSCEAR, was also applied in order to corroborate the experimental results. In this case, the radon exhalation rate was determined through the ^{226}Ra concentration from phosphogypsum, the real density and total porosity of phosphogypsum. This model is used for the evaluation of the flux density of ^{222}Rn at a surface of dry soil, according to the following equation:

$$J_D = C_{Ra} \cdot \lambda_{Rn} \cdot f \cdot \rho_s \cdot (1 - \varepsilon) \cdot L$$

Bulk density, real density and total porosity and Rn-222 exhalation rate from Cubatão and Uberaba phosphogypsum stacks

SAMPLING LOCATION	Bulk density (g·cm-3)	Real density ($g \cdot cm^{-3}$)	Total porosity (%)	^{222}Rn exhalation rate ($Bq\ m^{-2}\ s^{-1}$) (Theoretical model)	^{222}Rn exhalation rate ($Bq\ m^{-2}\ s^{-1}$) Experimental
Cubatão Radio 226 = 308 – 324 Bq/kg	1.21	2.40	49.6	0.161	0.083 - 0.102
	1.20	2.63	54.4	0.155	0.195 – 0.214
	1.20	2.39	49.7	0.156	0.268
	1.20	2.69	55.4	0.152	0.119
mean ± standard deviation				0.156 ± 0.004	0.164 ± 0.073
Uberaba Radio 226 = 291– 357 Bq/kg	0.76	2.64	71.1	0.092	0.070 – 0.073
	0.76	2.38	67.9	0.086	0.051 – 0.053
	0.76	2.50	69.6	0.111	0.091 – 0.098
	0.75	2.50	69.9	0.090	0.082 – 0.115
mean ± standard deviation				0.094 ± 0.011	0.079 ± 0.022

- The results obtained for the radon exhalation rate obtained experimentally and with the UNSCEAR model are quite similar.

- Although the Ra-226 activity concentration of phosphogypsum from Uberaba and Cubatão installations are similar, the corresponding radon exhalation rate are different, showing that the **porosity plays an important role in the exhalation of the radon gas**.

Internal exposure in dwellers due to inhalation of Rn

Exhalation of radon from phosphogypsum bricks and plaster obtained by a theoretical model

Bricks and Plates made of phosphogypsum

The radon exhalation rate from bricks and plates, made of phosphogypsum from three installations of the Vale Fertilizantes industry: Cubatão, Uberaba and Cajati, was evaluated by using theoretical model from UNSCEAR for building material, through the ^{226}Ra concentration:

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

Internal exposure in dwellers due to inhalation of Rn

Exhalation of radon from phosphogypsum bricks and plaster obtained experimentally

Phosphogypsum bricks and accumulation chamber / phosphogypsum plates and accumulation chamber / CR-39 radon dosimeter / Track density measurements system

The radon exhalation from bricks and plates was also determined experimentally by using the CR-39 method. The practical approach consisted of measuring the radon exhalation rate directly from the surface of the material to allow radon to build up in a container over time. The device used to this practical radon measurement was the accumulator.

Radon exhalation rate from bricks and plates made of phosphogypsum and other construction materials (Bq m^{-2} h^{-1})

Building Material	^{222}Rn exhalation rate	Reference
Phosphogypsum Stack	341 – 562	our results (Theoretical model)
Phosphogypsum Stack	284 – 590	our results (activated charcoal method)
Gypsum Brick	0.08 – 0.29	our results (CR-39 method)
Phosphogypsum Brick	0.03 – 1.89	our results (CR-39 method)
Phosphogypsum Brick	0.41 – 5.67	our results (Theoretical model)
Phosphogypsum Brick	6 – 10	Fournier et al., 2005
Gypsum Plate	0.2 – 18.4*	Folkerts et al., 1984
Phosphogypsum Plate	0.14 – 1.30	our results (CR-39 method)
Phosphogypsum Plate	0.16 - 4.30	our results (Theoretical model)
Phosphogypsum Plate	2.2 - 4.8	Lettner & Steinhäusler, 1988
Crude Brick	0.16	Sharma & Virk, 2001
Granite	0.16 - 1.42	Kotrappa & Stieff, 2009
Cement	0.27 - 0.66	Lettner & Steinhäusler, 1988
Cement	0.18 – 0.91	Sharaf et al., 1999
Concrete	4.32	De Jong et al., 2006
Soil	2.2 - 2.8	Rehman et al., 2006
Sand	3.9 - 16.7	Rehman et al., 2006
Slate	0.36 - 1.92	Chen et al., 2010

* Phosphogypsum

- The results obtained experimentally for the radon exhalation rate from plates and bricks made of phosphogypsum are of the same order of magnitude than those from conventional building materials. So, it can be concluded that the plates and bricks manufactured with phosphogypsum from these producers may be used as a building material, posing no additional health risk to dwellers due to radon exhalation rate.

- **The recycling of phosphogypsum for building materials manufacturing can be a safe alternative, considering its radon exhalation rate.**

Internal and external exposure in dwellers

Theoretical evaluation

The external and internal exposure in dwellers due to gamma irradiation can be evaluated by applying radium equivalent activity and external and internal hazard indices from bricks and plates made of phosphogypsum. The radium equivalent activity was obtained by the equation:

$$C_{Ra,eq} = C_{Ra} + 1.43 C_{Th} + 0.077 C_{K}$$

External hazard index was calculated using the following equation:

$$\frac{C_{Ra}}{370} + \frac{C_{Th}}{259} + \frac{C_{K}}{4810} \leq 1 \quad \text{for external exposure}$$

$$\frac{C_{Ra}}{185} + \frac{C_{Th}}{259} + \frac{C_{K}}{4810} \leq 1 \quad \text{for internal exposure}$$

Internal and external exposure in dwellers

Theoretical evaluation

Radium equivalent activities in Bq kg^{-1} ($C_{Ra,eq}$) and external and internal hazard indices

SAMPLE	$C_{Ra,eq}$	HAZARD INDICES	
		ext.	int.
bricks (Cubatão)	780	2.1	3.2
bricks (Uberaba)	559	1.5	2.3
bricks (Cajati)	84	0.2	0.3
plates (Cubatão)	755	2.0	3.1
plates (Uberaba)	512	1.4	2.2
plates (Cajati)	55	0.2	0.2

The results of radium equivalent, external and internal hazard indices showed that plates and bricks from Cubatão and Uberaba present values above the recommended limits, suggesting the application of a **more realistic scenario** for the evaluation of the exposure in dwelling for the safe application of phosphogypsum as building material.

EXPERIMENTAL HOUSE

The Experimental House

- In order to assess the feasibility of using phosphogypsum as building material, an experimental house was built with phosphogypsum plates of different origins.

- The house was entirely lined with phosphogypsum and designed to perform a comprehensive radiological evaluation, including the modeling of the external dose indoors, measurement of the external gamma exposure and of radon concentrations.

The Experimental House

- The plates were manufactured with phosphogypsum from different producers, located in in Cubatão, Cajati and Uberaba.
- At the house a bedroom and bathroom were built with phosphogypsum plates from Cubatão and other bedroom was built with Cajati phosphogypsum plates.

The Experimental House

In this experimental house it was possible to evaluate the dose conversion factors for the external exposure and to evaluate the real annual increment in the effective dose to an inhabitant of the house, which was below the 1mSv limit for every reasonable scenario.

The radon measurements were carried out over a period of 18 months, in order to determine the long-term average levels of the indoor radon concentrations. The radon concentrations varied from 45 to 50 Bqm^{-3} in the bedroom built with phosphogypsum plates from Cajati and from 83 to 119 $Bq\ m^{-3}$ in the bedroom and bathroom built with phosphogypsum from Ultrafertil.

The results obtained are below 300 $Bq\ m^{-3}$, the recommended investigation level for radon by ICRP in dwellings. It should be observed that the radon concentration results took into account the radon from soil under the construction.

The results obtained for the radon concentration in dwelling made of phosphogypsum is comparable to the radon concentration in conventional building material houses.

CONCLUSIONS

Main conclusion

The use of building materials with elevated or technologically enhanced levels of natural radioactivity could be a reason of higher external and internal doses for residents.

However, the results obtained in this study for activity concentrations and radiation doses gave evidence that the use of the Brazilian phosphogypsum as a building material poses no additional health risk to dwellers for the studied scenario.

There is a great advantage of using an actual dwelling built with phosphogypsum-based materials for the specific purpose of carrying out a radiological evaluation, considering the radioactivity contents and realistic room modeling by using detailed panel specifications, rather than reference rooms, to forecast external and internal doses.

The dose assessment based on a real scenario, where a given material is used in a specific way provides realistic conclusions, that can help in making decisions about the applicability of new materials. The methodology developed in this work can be applied to other studies and building materials by using appropriate adjustments.

Final remarks

Considering the important role of recycling abundant industrial residue and preserve natural sources for a sustainable development, it is encouraged to use phosphogypsum instead of natural gypsum as construction material.

The research carried out concerning the use of Brazilian phosphogypsum as construction material gave evidence that its application is safe from the radiological protection perspective and is economically feasible.

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