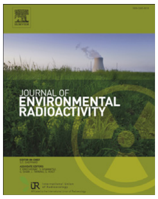
Journal of Environmental Radioactivity 132 (2014) 81–88

Contents lists available at ScienceDirect

Journal of Environmental Radioactivity

journal homepage: www.elsevier.com/locate/jenvrad



Assessment of radiological hazard of commercial granites from Extremadura (Spain)

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ARTICLE INFO

Article history:
Received 8 October 2013
Received in revised form
16 January 2014
Accepted 3 February 2014
Available online 4 March 2014

Keywords:
Granite
External irradiation
Radon
Exhalation
Uranium
Radium

ABSTRACT

The term “commercial granite” comprises different natural stones with different mineralogical components. In Extremadura, western Spain, “commercial granites” can be classified in three types: granite *s.s.* (*sensus stricti*), granodiorite, and diorite. The content of naturally occurring radionuclides depended of the mineralogy. Thus, the ^{40}K content increased as the relative content of alkaline feldspar increased but decreased as the plagioclase content increased. The radioactive content decreased in the following order: granite *s.s.* > granodiorite > diorite. In this work, the radiological hazard of these granites as building material was analyzed in terms of external irradiation and radon exposure. External irradiation was estimated based on the “*I*” index, ranged between 0.073 and 1.36. Therefore, these granites can be use as superficial building materials with no restriction. Radon exposure was estimated using the surface exhalation rates in polished granites. The exhalation rate in granites depends of their superficial finishes (different roughness). For distinct mechanical finishes of granite (polish, diamond sawed, bush-hammered and flamed), the surface exhalation rate increased with the roughness of the finishes. Thermal finish presented the highest exhalation rate, because the high temperatures applied to the granite may increase the number of fissures within it. The exhalation rates in polished granites varied from 0.013 to 10.4 Bq m^{-2} h^{-1}.

1. Introduction

Natural stone is an excellent building element, used for centuries thanks to its technical and aesthetic characteristics. It is a natural product that after an industrial process is suitable for use as a building material, without altering its composition, texture or physicochemical/physicomechanical characteristics. The term “commercial granites” comprises a wide number of different natural stones with different mineralogical classifications and particle textures. From a purely commercial point of view, the term granite is extended to all granular rocks lacking carbonate, which support grinding. Therefore, this term is used commercially to identify different geological materials such as gneiss, diorite, granodiorite and other rocks. According to their geological origin, granite is a rock formed under the Earth’s crust from a liquid magma. It is mainly composed of quartz, feldspar and mica; mineralogically it can vary widely depending on the geology and origin. This mineralogical variety gives these materials the possibility of presenting different colours and textures. One of the great attractions of ornamental rocks is that they can support different surface finishes. These surface finishes can create significant changes in the appearance and texture of the same type of natural stone.

The distribution of uranium in the Earth’s crust is related to magmatic activity during the formation of the Earth. The concentrations of uranium, thorium and potassium are generally higher in the granitic rocks, granitic pegmatites and syenites, and are closely related to mineralogical composition and petrographic characteristics (Ivanovich and Harmon, 1982). Uranium is found in rocks of different mineral species (like apatite, sphene and zircon) as a secondary/accessory mineral, or it can form its own minerals. Uranium distribution in rocks is linked to isomorphous mineral substitution, adsorption or inclusion process (Pertlik et al., 1974). Biotite (“black mica”) contains between 19% and 22% of the total uranium because it may contain inclusions of minerals rich in this element, such as zircon. Heavy minerals such as zircon, monazite, apatite, magnetite, ilmenite and riebeckite, contain between 61% and 65% of the uranium in a rock (Moreira-Nordemann, 1977).

The use of building materials from natural stone containing an enhanced content of naturally occurring radionuclides can pose a

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http://dx.doi.org/10.1016/j.jenvrad.2014.02.004

radiological hazard to the users of buildings containing these material. External irradiation and inhalation of radon emanating from these materials are main pathways of exposure. There are several indices that consider the contribution of all γ-emitter radionuclides of the natural series and ^{40}K, and parametric values according to different radiological criteria. The RP-112 (EU, 1999) defined the activity concentration index, I, and established limits for different uses of the building materials in order to assure the radiological protection of the population. Exposure to radon inhalation is regulated by its specific activity in indoor air in working places and houses (ICRP, 1993; IAEA, 2003).

The extraction of natural stone in Extremadura, western Spain, represents over 70% of the mining industry in this region. It is the second most important national producer in granite mining and third in slate quarrying. Granites and slates produced in Extremadura are exported to European Union countries, USA, Middle East, Japan and Australia. The main objective of the present paper is the assessment of the possible radiological hazard of commercial granites from Extremadura, taking into account the two main exposure pathways: external irradiation ("I" index) and radon inhalation (surface exhalation).

2. Material and methods

2.1. Determination of radionuclides by γ-spectrometry

Aliquots of granite samples were ground to particle size between 0.1 and 0.25 mm. These were oven-dried for 48 h to remove moisture and then put into 191 -cm^3 Petri-type capsules and sealed to avoid loss of any ^{222}Rn emanations. After 28 days to allow ^{226}Ra to reach secular equilibrium with its descendants, the samples were assayed by gamma spectrometry using an HPGe detector of 43% relative efficiency, with a peak-Compton ratio of 56:1 referred to the 1332.5 keV emission of ^{60}Co. The ^{214}Pb, ^{214}Bi, ^{228}Ac, and ^{40}K contents were systematically assayed in all samples. The ^{226}Ra content was determined in equilibrium with its descendants ^{214}Pb and ^{214}Bi. The ^{232}Th was assumed to be in equilibrium with ^{228}Ac.

2.2. Uranium determination

The granite samples were acid digested with a mixture of HNO_3, HCl, and HF (9:3:6 mL) in a microwave oven (Ethos Pro Milestone Ltd.) at 200 °C for 20 min prior to the corresponding radiochemical procedure. After digestion, the samples were evaporated to dryness and H_3BO_3 was added to eliminate fluorides. A known amount of ^{232}U was added as tracer. Then the uranium content was coprecipitated with $Fe(OH)_3$. The precipitate was re-dissolved in HCl 9M, followed by separation in a column with Dowex 1 × 4 resin. The uranium is retained in the column, and subsequently eluted with HNO_3 8M. Finally, the alpha sources were prepared by coprecipitation with NdF_3 (Sill, 1987).

2.3. Radium determination by α-spectrometry

Prior to the determination of the radium content, the granite samples were acid digested in the same way as for the uranium determination. The radium content in the sample was absorbed in MnO_2 precipitate. ^{133}Ba was added as tracer. Then the precipitate was dissolved in HNO_3 5M, and the uranium and thorium present in the samples were extracted with TBP (tributyl phosphate). Lastly, the radium was co-precipitated as $Ba(Ra)SO_4$ (Baeza et al., 1998). The recovery was determined by γ-spectrometry of the ^{133}Ba (302.85 and 356.01 keV) content of the corresponding sources.

2.4. Quality controls

Alpha spectrometric analyses of uranium and radium samples were carried out using twelve different silicon detectors with a mean efficiency of 23.2% and a resolution of 38.7 keV for a source-detector distance of 6 mm.

The overall quality control of these radiochemical procedures is guaranteed by the accreditation of the laboratory to carry out radioactivity assays in water, soil, and sediments according to UNE-EN ISO/IEC 17025 (ISO, 2005). Different reference materials were also used to check the quality of the measurements: IAEA-447 for uranium and IAEA Soil 6 for γ-spectrometry, and ^{226}Ra determined by α-spectrometry.

2.5. Radon exhalation

The radon exhalation was determined by means of the accumulation method described in the ISO/FDIS 11665-7 (ISO, 2012a). The accumulation container has cylindrical shape with 5.88 ± 1% L volume and 530.9 cm^2 open surface. The container had two orifices which were available for continuous air circulation, and was coupled to the measurement device, AlphaGuard (Saphymo GmbH). The air circulation was maintained using an AlphaPump, which was operated at a low flow-rate to avoid actively sucking radon from the sample. All granite slabs measured had greater dimensions than the container surface area.

2.6. Determination of rock parameters

The mineral content and the textural relationships within the rock are described in detail in a petrographic description. Rock fragments were glued on glass and roughened successively until 30 μm thick, for analysis under the microscope. Microscopic analysis entails mineral identification (major, secondary and accessory minerals) and textural description (shape, size and relationship between mineral grains, etc.) (AENOR, 2007).

The surface finishes have little influence on the mechanical behaviour of the materials, except for the surface roughness and rock porosity. The superficial roughness is a variable with an important influence on radon exhalation rates. The most common finishes traditionally used for the granites have been analyzed in this work (polish, thermal, diamond saw and bush-hammered). They can be classified according to its use indoors or outdoors. Polish finish is the most used indoor finish. It consists of polishing the granite until it has a highly reflective mirror gloss appearance. Polishing seals surface pores (adding durability) and is therefore nearly impervious to chemical wear and weather (by reducing the stone's porosity). The most common finishes for outdoor use are thermal finish, diamond saw, and bush hammered. Thermal finish is produced by applying a high-temperature flame to the surface of the stone (about 1100 °C), which causes the surface to exfoliate with the outermost grains flaking off (fracturing crystals on the face) leaving a rough textured surface finish suitable for slip resistant external paving. Diamond sawed finish is produced by sawing the granite slab with a diamond saw. Bush-hammered finish is the result of the repeated bush hammer impact (grid of conical or pyramidal points at the end of a large metal slug) on the granite surface. It creates a rough, pockmarked texture that resembles naturally weathered rock.

The surface roughness in the different granite finishes was determined by a Mitutoyo SJ-201 profilometer and using confocal interferometry light microscopy for optical quality control on surfaces (roughness, reflectivity, form, planarity and other parameters) SENSOFAR PLμ 2300 according to ISO 257178-2 (ISO, 2012b).