



Environmental impact of a granite processing factory as source of naturally occurring radionuclides



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ABSTRACT

The extraction and processing of ornamental stone, and granite in particular, generates a huge amount of wastes, which are usually disposed into slag heaps and subjected to weathering. Granite can present high content of naturally occurring radionuclides (^{40}K , $^{226,228}\text{Ra}$, $^{234,238}\text{U}$, ^{210}Po , and $^{228,230,232}\text{Th}$). A small-scale granite processing company was selected, and the generated wastes, mainly scraps and slurries, presented almost the same activity levels, since only physical processes (cutting) were used. Uranium and ^{40}K content in the water used in the factory as coolant were enhanced regarding its original value, as a consequence of its contact with the slurries. Other physico-chemical parameters of the water (pH, conductivity, Cl, K, Na, Mg) also increased. The environmental behavior of naturally occurring radionuclides contained in solid wastes, scraps and slurries, were assessed by means of a sequential extraction procedure. Uranium in scraps and slurries was mainly associated with diluted-acid (HCl 1 M), concentrated-acid (HCl 6 M), and residual fractions; while ^{40}K was almost exclusively associated with the residual fraction. The readily bioavailable fraction (water soluble + exchangeable) in scrap and slurry were lower than 20%, and decreased in the following order: $^{226,228}\text{Ra} > ^{234,238}\text{U} > ^{40}\text{K} \gg ^{210}\text{Po} \approx ^{228,230,232}\text{Th}$.

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1. Introduction

The extraction and transformation processes of natural stone generate a significant amount of sterile material of different particle size (from blocks to mud). During the granite production, from its extraction from the quarry to its final use, considerable amounts of wastes are generated. The quantity of waste for silicate materials exceeds 30% of the raw material and can reach 40% (OSNET, 2004). The management of these wastes is a major task for granite processing companies. The processing waste can be classified in three main categories depending on its size (OSNET, 2004):

- Large to medium size waste called scrap. This kind of waste can have a size of several centimeters and comes from broken or defective slabs whose surface might be polished.
- Medium to small size waste consisting of splints, flakes, chips which are created during trimming of blocks or slabs.
- Small size waste consisting of fine particles and has the form of dust or slurry. Slurry is created from all stone cutting operations when the cooling water mixes with the fine stone particles. It is collected and recycled in appropriate installments in order to

recycle the water into the production process. Using press filters the water recovery can reach up to 90% still leaving a material called slurry with a high humidity content (22–28%).

Waste generation is one of the major problems in most industrial sectors, becoming one of the keys that hinders the ornamental stone sector development, and granite in particular. The thicker materials are crushed for use as aggregate in order to reduce their environmental impact, or accumulated in slag heaps to be rehabilitated. The finest materials generated during the cutting process or finish treatment, are mobilized through the water (recycling system), resulting an increase in suspended solids in water used in the process. Slurries are thickened (dewatered) to reduce the volumes transported off-site for disposal. This process produces a large amount of slurry (siliceous nature in the case of granite).

Natural stone, and granite in particular, can present high content of naturally occurring radionuclides due to its mineralogical composition and petrographic characteristics. Uranium is found in rocks of different mineral species (like apatite, sphene and zircon) as a secondary/accessory mineral. Biotite, monazite, magnetite, ilmenite, and riebeckite present also high uranium content (Moreira-Nordemann, 1977). The content of the naturally occurring radionuclides in granite were within the ranges (5–282), (2.2–133), and (37–1633) Bq/kg for ^{226}Ra , ^{232}Th , and ^{40}K respectively for Spanish granites (CSN, 2004; Guillén et al., 2014).

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Uranium content in granites from our region was within the range (5–404) and (5–375) Bq/kg for ^{238}U and ^{234}U respectively (Guillén et al., 2014); and within the range (19–666) Bq/kg for ^{238}U for other countries (Aarafa, 2004; Pavlidou et al., 2006).

The granite processing industry generates a huge amount of wastes, which contains naturally occurring radionuclides. Therefore, the main goal of this study is to assess the possible radiological impact of this kind of industry into the environment. In order to do it, a Small-Size Company (granite quarry and processing plant) was selected and the naturally occurring radionuclide content of the wastes generated was determined. The area considered for our study is a granite batholith with many small, family-owned companies in the ornamental stone-mining, quarrying and processing sector. Ornamental stone sector keep a large production capacity in the region, even though the volume of material produced has fallen substantially in recent years due to lower market demand. Current production from this area was estimated to be around 265,000 tons of material produced (final product) in 2013. This production generates a significant volume of scrap (119,250 tons) and slurry (26,500 tons). The management of this amount of wastes affects the environment. They are usually collected and deposited into dumpsites, subject to weathering. Also during the extraction and transformation processes, companies consume about 10,000 L/day of water as coolant. The wastes considered in the study were scrap, slurry, and water (before and after its use as coolant during the granite transformations process). Two sampling campaigns were carried out in order to observe seasonal variations in the water recycling system in the granite processing plant: the first one at the end of the winter (March 2011), the second one in autumn (November 2011, after an especially dry summer in this region).

2. Material and methods

2.1. Sample pre-treatment

To determine total concentrations of $^{234,238}\text{U}$, ^{226}Ra , and $^{228,230,232}\text{Th}$ in solid samples, they were dried at 100 °C for at least 24 h to eliminate their free water content. Then, they 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. For ^{210}Po , an aliquot of 1 g d.w. of sediment was digested with HNO_3 and H_2O_2 (8:2 mL) in a microwave oven at 180 °C for 20 min. The sample was filtered and converted to HCl medium.

Due to the great number of particles suspended in the water collected from the pond, these samples were filtered through a filter with 0.45 μm pore size. Then, two fractions were considered: (i) radionuclides in the suspended matter retained in the filter, and (ii) radionuclides remaining in solution.

2.2. Determination of radionuclides by γ -spectrometry

Naturally occurring radionuclides ^{228}Ra (and also ^{226}Ra in solid samples) and ^{40}K were determined by γ -spectrometry samples were oven-dried for 48 h to remove moisture. They were then put into 191-cm³ 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, and energy resolution of 2 keV. ^{228}Ra was considered to be in equilibrium with ^{228}Ac . It was associated to an Ortec DSPEC module which controls the power supply and the electronics.

Finally the spectrum was collected by Ortec Gammavision software. The calibration of the detector was carried out using a certified solution from NPL, containing ^{241}Am , ^{109}Cd , ^{57}Co , ^{131}Ce , ^{51}Cr , ^{113}Sn , ^{85}Sr , ^{137}Cs , ^{65}Zr , ^{60}Co , and ^{88}Y . The efficiency was calibrated for many types of geometry, typically used in our routine measurements, by adding known quantities of the certified solution to bulk material. Fig. 1 shows a typical γ -spectrum for a granite sample.

2.3. Radiochemical procedures (U, Ra, Po, and Th)

To determine uranium content, ^{232}U was first added as tracer. Then, uranium was co-precipitated with $\text{Fe}(\text{OH})_3$. The precipitate was re-dissolved in HCl 9 M, followed by separation in a column with Dowex 1 \times 4 resin. Uranium is retained in the column, and subsequently eluted with HNO_3 8 M. Finally, the alpha sources were prepared by co-precipitation with NdF_3 (Sill, 1987). Radium content in the water was absorbed in MnO_2 precipitate. ^{133}Ba was added as tracer. Then the precipitate was dissolved in HNO_3 5 M, and uranium and thorium present in the samples were extracted with TBP (tributyl phosphate). Lastly, radium was co-precipitated as $\text{Ba}(\text{Ra})\text{SO}_4$ (Baeza et al., 1998). The recovery was determined by γ -spectrometry of the ^{133}Ba (302.85 and 356.01 keV) of the corresponding sources, using a germanium N-type detector with a 25% relative efficiency, a 1.87 keV resolution for the 1332 keV ^{60}Co peak, and a peak-to-Compton ratio of 57.5:1.

In the determination of ^{210}Po content, ^{209}Po was used as tracer. Polonium content was co-precipitated with $\text{Fe}(\text{OH})_3$. Then the precipitate was dissolved in HCl 8 M and diluted to HCl 1.5 M. Polonium was autodeposited onto silver planchets, and measured by alpha spectrometry (Bolívar et al., 2002). Thorium content was also co-precipitated with $\text{Fe}(\text{OH})_3$, with ^{229}Th as tracer. The precipitate was dissolved in HNO_3 8 M and passed through a column filled with Dowex 1 \times 8 resin. Thorium is retained in the column and was eluted with concentrated HCl . The thorium source was prepared by co-precipitation with NdF_3 .

2.4. Alpha spectrometry

Alpha spectrometries of uranium, radium, thorium, and polonium 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. In order to minimize the risk of contamination of the detector by alpha recoil, they are used to measure the same type of radiochemical alpha sources. The calibration was carried out by using a certified source of ^{233}U , ^{239}Pu , and ^{241}Am . Activity levels were determined in mBq/L, but are easily converted to concentration units in $\mu\text{g/L}$ using the following factors: ^{238}U ($8.03 \cdot 10^1$); ^{234}U ($4.34 \cdot 10^{-3}$); ^{226}Ra ($2.73 \cdot 10^{-5}$); ^{210}Po ($6.01 \cdot 10^{-9}$); ^{232}Th ($2.46 \cdot 10^2$). Associated uncertainties were estimated using the 2σ criterion. Fig. 2 shows typical α -spectra for the radiochemical separations carried out in the present study.

The overall quality control of these radiochemical procedures is guaranteed by the accreditation of the laboratory to carry out radioactivity assays in environmental samples according to UNE-EN ISO/IEC 17025 (ISO, 2005). Different reference materials were also used to check the quality of the measurements: IAEA-381 for uranium, IAEA Soil 6 for radium and γ -spectrometry, and IAEA-327 for thorium and polonium.

2.5. Sequential speciation procedure

The sequential speciation procedure used in the present work was based on techniques frequently used to test agriculture soils (Pavlotskaya, 1974; Krouglov et al., 1998). The fractions considered

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