Journal of Radioanalytical and Nuclear Chemistry, Vol. 267, No.3 (2006) 669–673

Radiometric analysis of Chinese commercial granites

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(Received September 14, 2005)

Due to the widespread use of granites as building and ornamental materials, measurements of ^{226}Ra, ^{232}Th and ^{40}K activities in commercial granites have been carried out using a NaI(Tl) γ-ray spectrometer with a matrix-inversion-based spectral stripping technique. The concentrations of ^{226}Ra, ^{232}Th and ^{40}K in Chinese commercial granite range from 14.5 to 204.7 Bq·kg^{-1}, 16.7 to 186.7 Bq·kg^{-1} and 185.7 to 1745.6 Bq·kg^{-1}, respectively. The mean values of the activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K in red and pink commercial granites are all higher than those in black and gray commercial ones. The radium equivalent activity (Ra_{eq}), the external hazard index (H_{ex}), the internal hazard index (H_{in}) and the annual gonadal dose equivalent (AGDE) were also calculated and compared to the international recommended values. Six types of red commercial granites (CBR, MLR, QXR, PBR, JXR, LQR, YDR and TSR) of China do not satisfy the universal standards.

Introduction

The naturally occurring radionuclides ^{226}Ra, ^{232}Th and ^{40}K are found to be present in significant amounts in soil, building materials and recycled industrial waste products.[1–4] The possible exposure to γ-radiation emitted from these radionuclides is not only confined to the outdoor environment but can also occur in houses, offices and other working places. The knowledge of the natural radioactivity of building materials is important for the determination of population exposure to radiations, as most of the residents spend about 80% of their time indoors. Building materials contribute to natural radiation exposure in two ways. First, by gamma-radiation, from ^{226}Ra, ^{232}Th, ^{40}K and their decay products to an external whole body dose exposure and secondly by radon exhalation to an internal dose exposure due to the deposition of radon decay products in the human respiratory tract.[5] Even though these radionuclides are widely distributed, their concentrations have been found to depend on the local geological conditions and as such they vary from place to place.[5] Therefore, it is important to measure the concentration of radionuclides in all building materials collected from different places and to assess the possible radiological risks to human health. The measurements will also help in the development of standards and guidelines for the use and management of these materials.

Commercial granite holds an important position in the Chinese building material market. There are 1000 big production sites of commercial granites in China in 1995. In China, granites are usually used as building and decorative materials. The commercial granite mines and production sites of China are mainly distributed in Fujian, Shandong, Guangxi, Guangdong, Jiangxi, Xinjiang and Shaanxi provinces. The main production series of Chinese commercial granites are red, pink, black and gray. The red and pink varieties are mainly luoyuan red, luzhong red, cherry blossom, peach blossom, tianshan red, maple leaf red, and so on. The black varieties are mainly neimongol black, jinan cyan, fujing black, and so on. The gray varieties are quanzhou gray and sesame white. Distinct types of commercial granites have different geological origins and mineralogical compositions and may be either magmatic or metamorphic rocks.[6] Concerning their compositions, granites are mixtures of minerals of visible multicolored grains. One-color grains are typically encircled by grains of other colors, e.g., gray quartz is close to pink orthoclase, white plagioclase and dark mica. Commercial granites contain feldspar (hardness 6 in Mohs scale) of various colors: white pink, red, yellow, brown, green and gray. Many granites, especially of light colors, contain quartz (hardness 7 in Mohs scale) with gray (sometimes bluish) color and the grains are glassy translucent without cleavage. Further, there are dark minerals such as hornblende, pyroxene and biotite with black, dark green or dark brown colors. These minerals have larger specific gravity and lower hardness than feldspars and quartz. Some granite contains garnet showing near round shape and brown to dark-red color.[7] The natural radionuclide contents of granites are intimately related to their mineral compositions and general petrologic features.[8–10]

In this paper, the concentration of ^{226}Ra, ^{232}Th and ^{40}K content of Chinese commercial granites has been estimated using γ-ray spectroscopy. The paper presents the results for the measured activities, the radium equivalent activity and the values of both the internal and external hazard indices and the annual gonadal dose equivalent (AGDE) associated with the usage of main commercial granites of China.

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0236–5731/USD 20.00

Akadémiai Kiadó, Budapest
Springer, Dordrecht

Experimental

Eighty one samples of 20 different types of the main Chinese commercial granites were collected from Xi'an and Baoji building stone markets. All rock samples were crushed and milled to a fine powder with a particle size less than 0.16 mm. Each sample was homogenized and dried in a temperature controlled furnace at 110 °C for 2–6 hours to remove moisture. After cooling, the dry materials (500±1 g) were sealed in gas-tight, radon impermeable, cylindrical polyethylene containers (10.5 cm diameter, 7.5 cm height). These samples were then left for 4–5 weeks to allow for Ra and its short-lived progeny to reach radioactive equilibrium.

The concentration of the natural radioactivity (^{226}Ra, ^{232}Th and ^{40}K) in the Chinese commercial samples were determined using a ∅ 12.5×10 cm^3 NaI(Tl) γ-ray spectrometric system.[4]

The spectra were collected for each standard material and background over 400-minute counting times each. The spectral windows were adjusted around the 1.46 MeV, 1.76 MeV and 2.62 MeV energy peaks. The sample counting time was also 400 minutes. Each sample was counted three-times before an average was taken. The integrated counts recorded under the energy peaks of 1.46 MeV, 1.76 MeV and 2.62 MeV were noted for each spectrum. The count rate in each of the three spectral windows is related to the concentrations of the radioactive elements in the standards by the following set of equations:[5]

$$R_{ij} = \sum (A_{ik} C_{ik}) + B_i \quad (1)$$

where R_{ij} is the count rate for the ith region of the jth standard, A_{ik} is the calibration coefficient and B_i is the background count rate.

Equation (1) can be expressed in a matrix form as:

$$[R]=[A][C]+[B] \quad (2)$$

where $[R]$ is a 3×1 matrix of the observed count rates, $[A]$ is a 3×3 matrix of the calibration coefficients, $[C]$ is a 3×1 matrix of the nuclide concentrations and $[B]$ is a 3×1 matrix of the background count rates.

Inverting the $[A]$ matrix can solve the above equation:

$$[C]=[A^{-1}]\{[R]-[B]\} \quad (3)$$

The activity mass concentration was calculated using the following relations:

$$C_K = A^{-1}\{R_K - B_K\}, \quad (4)$$

$$C_{Ra} = A^{-1}\{R_{Ra} - B_{Ra}\}, \quad (5)$$

$$C_{Th} = A^{-1}\{R_{Th} - B_{Th}\}. \quad (6)$$

The spectra of potassium, the uranium series and the thorium series overlap. Each spectral window chosen to detect a particular radionuclide contains contributions from the other two radionuclides. Using the spectral stripping technique,[11] the necessary corrections for this spectral overlap were made.

The matrix $[A]$ in Eq. (2) was determined from the known activity concentration of the standard material and the count rates of the specified windows after background subtraction. The inverse matrix A^{-1} was found and used for determination of the unknown activity concentration.

Results and discussion

The measured activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K in various commercial granites are given in Table 1. As shown in the table, the activity concentrations in Chinese commercial granite samples varied from 14.5 to 204.7 Bq·kg^{-1} for ^{226}Ra, from 16.7 to 186.7 Bq·kg^{-1} for ^{232}Th and from 185.7 to 1745.6 Bq·kg^{-1} for ^{40}K, respectively. The concentration of ^{226}Ra, ^{232}Th and ^{40}K of commercial granite of various colors are different. The natural radionuclide concentration varied with the production site of the commercial granite. The activity concentrations range from 14.5 to 204.7 Bq·kg^{-1} with an average of 88.4 Bq·kg^{-1}, 30.5 to 186.7 Bq·kg^{-1} with an average of 114.1 Bq·kg^{-1} and 931.5 to 1745.6 Bq·kg^{-1} with an average of 1270.3 Bq·kg^{-1} for ^{226}Ra, ^{232}Th and ^{40}K, respectively, in red and pink commercial granites and range from 16.5 to 34.2 Bq·kg^{-1} with an average of 24.2 Bq·kg^{-1}, 16.7 to 36.9 Bq·kg^{-1} with an average of 29.0 Bq·kg^{-1} and 185.7 to 1354.6 Bq·kg^{-1} with an average of 768.6 Bq·kg^{-1} for ^{226}Ra, ^{232}Th and ^{40}K, respectively, in black and gray commercial granites. The mean values of the activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K in red and pink commercial granites are all higher than those in black and gray ones.

Activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K in the commercial samples produced in China have been compared in Table 2 with those for various granites.[6] The measured average activities of ^{226}Ra, ^{232}Th and ^{40}K in red and pink commercial granites are almost equal to the mean values of ^{226}Ra, ^{232}Th and ^{40}K in acidic granite. The measured average activities of ^{226}Ra, ^{232}Th and ^{40}K in black and gray commercial granites are in the range of the natural radionuclide concentrations of basic granite, ultra-basic granite and intermediate granite. The lithology of the red and pink commercial granites is mostly acidic granite, and of the black and gray commercial granites is mainly basic, ultra-basic and intermediate granites.[6]

Table 1. Activity concentration of ^{226}Ra, ^{232}Th and ^{40}K in the Chinese commercial granites (in Bq·kg^{-1})

Commercial name	Production site	Number of samples	^{226}Ra	^{232}Th	^{40}K
Luoyuan red (LYR)	Fujian	4	70.5 ± 10.3	76.6 ± 18.6	1425.6 ± 32.5
Yongding red (YDR)	Fujian	6	108.4 ± 23.7	75.6 ± 17.3	1445.1 ± 60.4
Luzhong red (LZR)	Shandong	3	62.5 ± 2.1	74.2 ± 5.6	953.4 ± 51.2
Luyuan red (LR)	Shandong	5	48.4 ± 9.3	76.2 ± 14.2	931.5 ± 41.2
Peach blossom red (PBR)	Guangdong	3	114.5 ± 21.1	186.4 ± 14.6	1415.3 ± 45.1
Cherry blossom red (CBR)	Guangdong	5	204.7 ± 25.1	116.5 ± 24.7	1015.6 ± 38.4
Fine flower red (FFR)	Guangdong	3	55.4 ± 16.3	81.5 ± 17.2	1175.6 ± 65.1
Sun red (SR)	Henan	2	14.5 ± 2.1	30.5 ± 4.2	1435.3 ± 45.6
Maple leaf red (MLR)	Guangxi	7	134.1 ± 37.2	152.3 ± 27.4	1415.3 ± 45.1
Tianshan red (TSR)	Xinjiang	6	56.4 ± 8.6	174.3 ± 26.5	1120.7 ± 37.4
Orient red (OR)	Zhejiang	3	36.5 ± 8.3	86.7 ± 13.4	1352.4 ± 36.2
Longquan red (LQR)	Zhejiang	2	98.4 ± 18.6	186.7 ± 14.7	946.7 ± 21.4
Qinxi red (QXR)	Zhejiang	4	124.5 ± 22.6	168.7 ± 27.5	1406.5 ± 48.2
Jiangxi red (JXR)	Jiangxi	8	108.7 ± 18.2	167.4 ± 24.2	1745.6 ± 55.3
Neimongol black (NB)	Neimongol	4	32.4 ± 3.5	16.7 ± 2.4	756.8 ± 24.7
Jinan cyan (JNC)	Shandong	3	26.5 ± 3.4	35.4 ± 7.6	1354.6 ± 36.2
Fujing black (FJB)	Fujian	3	24.6 ± 2.5	32.7 ± 3.5	345.6 ± 2.1
Black jade (BJ)	Zhejiang	2	26.4 ± 2.1	36.5 ± 4.3	564.2 ± 28.2
Quanzhou white (QZW)	Fujian	5	18.6 ± 1.3	28.3 ± 2.6	185.7 ± 4.6
Water lily green (WLG)	Hebei	3	16.5 ± 1.7	24.3 ± 2.3	204.6 ± 14.2

Table 2. Range of activity concentration of ^{226}Ra, ^{232}Th and ^{40}K in different type granites of China (in Bq·kg^{-1})[6]

Rock	^{226}Ra			^{232}Th			^{40}K		
	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean
Basic and ultra-basic granite	4.0	25.4	9.6	0.5	53.5	13.6	17	787	353
Intermediate granite	20.9	155	52.1	3.2	201	69.6	281	1618	941
Acidic granite	6.3	374	79.6	9.8	276	99.9	446	1810	1128
Alkaline granite	53.7	200	126.9	65.8	252	158.9	2419	3357	2920
Red and pink commercial granite*			88.4			114.1			1270.3
Black and gray commercial granite*			24.2			29.0			768.6

* From the present study.

To represent the activities duo to ^{226}Ra, ^{232}Th and ^{40}K by a single quantity which takes into account the radiation hazard association with them, a common index called the radium equivalent activity (Ra_{eq}) has been introduced, defined as:[5,12,13]

$$Ra_{eq} = C_{Ra} + 1.43C_{Th} + 0.077C_K \quad (7)$$

where C_{Ra}, C_{Th} and C_K are the activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K in Bq·kg^{-1}, respectively. While defining Ra_{eq}, it has been assumed that 1 Bq·kg^{-1} of ^{226}Ra, 0.7 Bq·kg^{-1} of ^{232}Th and 13 Bq·kg^{-1} of ^{40}K produce the same γ-ray dose.[5,12,13] The radium equivalent activity Ra_{eq} for Chinese commercial granite ranges from 67.0 to 490.0 Bq·kg^{-1} as shown in Fig. 1. The mean value of Ra_{eq} for red and pink commercial granite and black and gray commercial granite is 349.4 and 124.9 Bq·kg^{-1}, respectively.

The external hazard index (H_{ex}) is defined as:[5,12,14]

$$H_{ex} = (C_{Ra}/370) + (C_{Th}/259) + (C_K/4810) \quad (8)$$

The value of this index must be less than unity for the radiation hazard to be negligible, i.e., for the radiation exposure due to radioactivity in construction materials to be limited to 1.5 mSv·y^{-1}. For the maximum value of H_{ex} to be less than unity, the maximum value of Ra_{eq} must be less than 370 Bq·kg^{-1}. The calculated values of H_{ex} for the commercial granite studied in this work range from 0.18 to 1.32 as show in Fig. 2. The values of H_{ex} of Chinese commercial granite studied in this work are less than unity except for CBR, MLR, QXR, PBR, JXR, LQR and TSR samples.

In addition to the external hazard, radon and its short-lived products are also hazardous to the respiratory organs. The internal exposure to radon and its daughter products is quantified by the internal hazard index (H_{in}) which is given by:[5,12,14]

$$H_{in} = (C_{Ra}/185) + (C_{Th}/259) + (C_K/4810) \quad (9)$$

For the safe use of a material in the construction of dwellings, H_{in} should be less than unity.[5] The calculated values of H_{in} range from 0.23 to 1.77 as show in Fig. 2. The values of H_{in} of CBR, MLR, QXR, PBR, JXR, LQR, YDR and TSR samples are higher than unity.

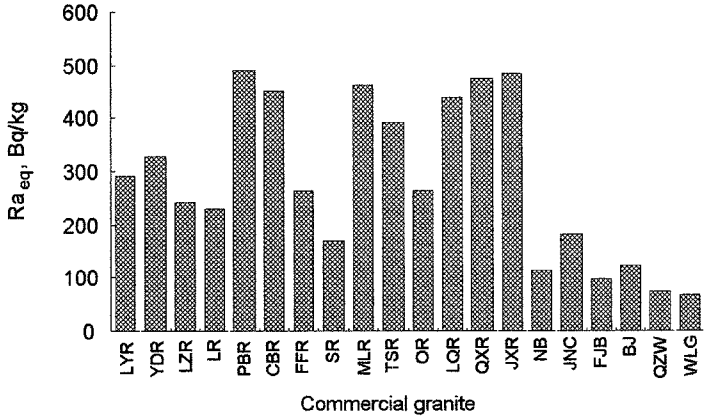

Fig. 1. Measured distribution of radium equivalent values in Chinese commercial granites

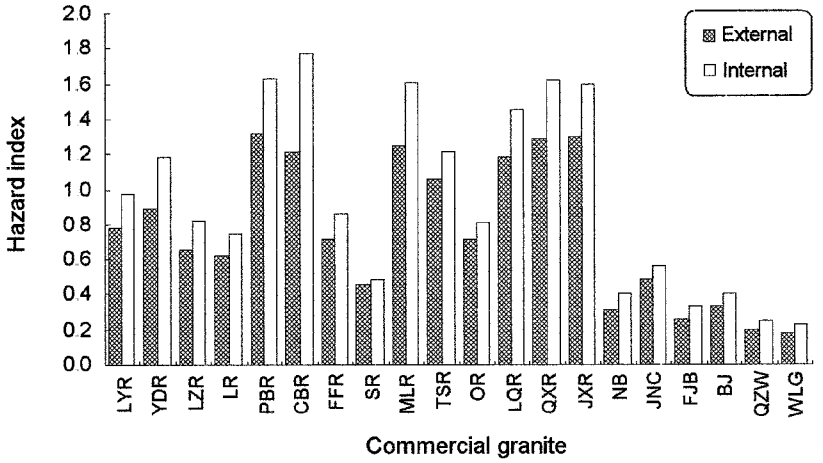

Fig. 2. Measured values of both the external and the internal hazard indices for Chinese commercial granites

Two similar indices (external exposure index I_{ex} and internal exposure index I_{in}) proposed to serve as a criterion in the People's Republic of China, which are defined as:[15]

$$I_{ex} = (C_{Ra}/370) + (C_{Th}/260) + (C_K/4200) \quad (10)$$

$$I_{in} = C_{Ra}/200 \quad (11)$$

This criterion, which only considers internal exposure, corresponds to a maximal ^{226}Ra activity concentration of 200 for the building materials. The values of external exposure index and internal exposure index for Chinese commercial granite studied in this work calculated by Eqs (10) and (11) range from 0.19 to 1.36 and 0.07 to 1.02, respectively. According to the Chinese criterion,[15] the CBR, PBR, JXR and QXR commercial granites can not be used as building and interior decorative materials of dwelling, while there are not any restriction for the use of other Chinese commercial granite.

The gonads, the active bone marrow and the bone surface cells are considered as the organs of interest by UNSCEAR (1988).[16] Therefore, the annual gonadal dose equivalent (AGDE, $\mu Sv \cdot y^{-1}$) due to the specific activities of ^{226}Ra, ^{232}Th and ^{40}K was calculated by:[9,17]

$$AGDE = 3.09C_{Ra} + 4.18C_{Th} + 0.314C_K \quad (12)$$

The obtained value of AGDE for the studied samples of Chinese commercial granite ranges from 0.22 to 1.58 $mSv \cdot y^{-1}$ as shown in Fig. 3. The values of AGDE of black and gray commercial granite studied in this work are found to be around the world average for soil (0.30 $mSv \cdot y^{-1}$).[17] However, the AGDE values of red and pink commercial granites studied are more than twice the world average values for soil.

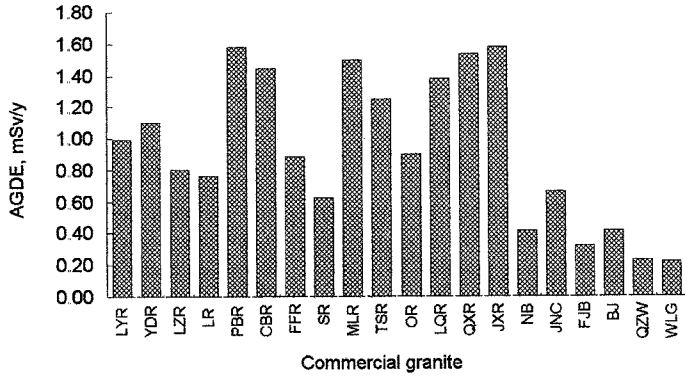

Fig. 3. Calculated values of AGDE for the studied samples of Chinese commercial granites

Conclusions

In view of worldwide concern about the radioactivity contents of various construction materials, measurements of the activity concentration of some Chinese main commercial granites have been carried out by using a NaI(Tl) detector along with a spectral stripping technique. The measured values of the activities of ^{226}Ra, ^{232}Th and ^{40}K in the samples of Chinese commercial granite have been found to lie in the range of 14.5 to 204.7 $Bq \cdot kg^{-1}$, 16.7 to 186.7 $Bq \cdot kg^{-1}$ and 185.7 to 1745.6 $Bq \cdot kg^{-1}$, respectively. The natural radionuclide concentration varied with color and production site. The mean values of the activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K in red and pink commercial granites are all higher than those in black and gray commercial granites. According to the Chinese criterion, four types of commercial granites (CBR, PBR, JXR and QXR) can not be used as building and interior decorative materials of dwelling. However, in the model proposed by BERETKA and MATHEW,[12] six types of red commercial granites (CBR, MLR, QXR, PBR, JXR, LQR, YDR and TSR) of China do not satisfy the universal standards (external and internal hazard index need to be less than unity). So, the safe use of these commercial granites should be noticed.

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The authors would like to thank Provincial Natural Sciences Foundation of Shaanxi and State Key Laboratory for Mineral Deposits Research of Nanjing University for their financial support. Gratitude is expressed to J. XIAOWEI, W. XIAOLEI, L. ZHENDONG for assisting in sampling.

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