Optimization of decay time in radioactivity detection of building ceramics and analysis of radioactivity level of ceramics in Nan’an city

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Abstract. The basic principle of radioactivity and the technical method for measuring the radioactivity of ceramic tiles with low background multi-channel high-purity germanium gamma spectrometer are introduced. The reasonable optimization of the balance time of tile radioactivity detection has certain reference value for improving the level of radioactivity detection technology. Combined with the data analysis of the special quality supervision and random inspection of ceramic tiles in the past five years, the radioactivity indicators of ceramic tile products in the jurisdiction are all at a qualified level, effectively eliminating the hidden dangers of radioactive safety of ceramic tile products and ensuring the health and safety of the citizens.

1. Introduction
Ceramic tile is an important decorative material in the field of construction industry. It’s raw materials are mixed with various mineral raw materials, such as gravel, clay, coal slag, phosphorous slag and other inorganic materials, which contain radionuclides: $^{226}\text{Ra}$, $^{232}\text{Th}$, $^{40}\text{K}$, which will cause radioactivity and endanger human health. At present, our country has issued a series of relevant standards such as GB 6566-2010 [1], CNCA-12C-050 2008 [2], SN/T 1570.2-2005 [3] to make detailed requirements on the radioactivity level of building materials. GB 6566-2010 is mainly used as the basis for radioactivity detection of building ceramic tiles. As the standard does not specify the balance time of the test sample, the testing institutions are different in this standard, which usually cause large deviation of the test results. So it is necessary to optimize the test balance time to promote the standardization and uniformity of testing work. The high purity germanium spectrometer has the advantages of good energy resolution, high detection efficiency, strong sensitivity and good reliability, it can be used to test the content of radionuclides in ceramic tiles and the level of radioactivity of ceramic tiles can be evaluated scientifically.

2. Principle of radioactivity testing

2.1. Basic principles of radioactivity
French physicist Henry Beckler first discovered and proposed the term radioactivity, which refers to the presence of unstable atomic nuclei that spontaneously emit certain rays. The nuclei of most substances in nature are in a stable state, but some unstable nuclides are unavoidable. These unstable nuclides are prone to produce isotopes with different neutron numbers, which form stable nuclei after spontaneous decay, and their decay processes simultaneously released particles and rays, mainly $\alpha$, $\beta$.
and γ rays\cite{4}. The process is called radioactive decay. In the building materials such as ceramic tiles, the radioactive materials mainly exist in the radionuclide radium, thorium and potassium. In theory, because the radiation dose of the γ radiator has a direct relationship with the specific activity of radioactivity, the specific activity value is used to determine the radioactivity levels of radium, thorium, and potassium. In practical applications, in order to facilitate the assessment of the level of radioactive harm to the human’s body, the internal and external exposure index values are used as the basis for judgment. Table 1 provides compare of interrelated national standards of ceramics in the internal and external exposure index. Table 2 shows Natural Radionuclide Limit of different country\cite{5}.

Table 1. The compare of interrelated national standards of ceramics in the internal and external exposure index.

| National standard                                      | Class A   | Class B   | Class C   |
|--------------------------------------------------------|-----------|-----------|-----------|
| GB 6566-2010 limit of radionuclide in Building materials | $I_{Ra} \leq 1.0$, $I_{γ} \leq 1.3$ | $I_{Ra} \leq 1.3$, $I_{γ} \leq 1.9$ | $I_{γ} \leq 2.8$ |
| CNCA-12C-050 2008 Compulsory certification of porcelain brick products\cite{4} | $I_{Ra} \leq 1.0$, $I_{γ} \leq 1.3$ | $I_{Ra} \leq 1.3$, $I_{γ} \leq 1.9$ | / |
| HJ/T 297-2006 Technical requirements for environmental labeling products\cite{5} | $I_{Ra} \leq 0.9$, $I_{γ} \leq 1.2$ | $I_{Ra} \leq 0.9$, $I_{γ} \leq 1.2$ | $I_{Ra} \leq 0.9$, $I_{γ} \leq 1.2$ |

Note: $I_{Ra}$—Internal exposure index. $I_{γ}$—External exposure index. Class A—Unlimited production, sales and use. Class B—Can not be used for interior decoration of Class I civil buildings, but can be used for interior decoration of Class II civil buildings, industrial buildings and exterior decoration of all other buildings. Class C—Can only be used for exterior decoration of buildings and other outdoor uses\cite{1}.

Table 2. Radionuclide limit of different country.

| Country or organization | $^{226}$Ra (Bq/kg) | $^{232}$Th (Bq/kg) | $^{40}$K (Bq/kg) |
|-------------------------|---------------------|--------------------|------------------|
| United Nations Scientific Committee on the Effects of Atomic Radiation | 370 | 260 | 4810 |
| China                   | 370 | 260 | 4200 |
| Finland                 | 300 | 200 | 3000 |
| Norway                  | 300 | 200 | 3000 |
| Luxembourg              | 350 | 250 | 5000 |
| Former Yugoslavia       | 400 | 300 | 5000 |
| Sweden                  | 1000 | 700 | 10000 |
| Austria                 | 1000 | 670 | 10000 |

2.2. High-purity germanium gamma spectrometer detection technology principle

The high-purity germanium gamma spectrometer uses high-purity germanium crystals as semiconductor detectors. The high voltage is applied through the metal contact pole. Under the action of an external electric field, the generated gamma rays interact with the electrons outside the crystal core to form electron hole pairs, the corresponding electrical signal generated and induced by the charge is recorded by the spectrometer electronics system to form a gamma spectrum\cite{6-8}. Different energy gamma rays produce different amounts of charge, which in turn affects the magnitude of the pulse amplitude. The multi-channel analyzer is used to perform energy calibration and efficiency calibration on the known nuclide, and the exact radiation information and nuclide activity value are obtained from the analysis software. The test system is composed of HPGe detector, high voltage power supply, amplifier, digital spectrometer, multi-channel analyzer and γ spectrum analysis software.
The system works as shown in Figure 1.

Figure 1. HPGe system diagram.

The specific activity of nuclide is calculated by the software analysis of the standard source spectrum and the full-energy peak area of each nuclide characteristic peak of the sample spectrum, and the peak area is divided by the measurement time to obtain the net-energy peak count rate \(^{(1-11)}\). Use formula (1) to calculate the specific activity of the nth nuclide in the tested sample \(C_j\), unit: Bq/kg.

\[
C_j = \frac{A_j - A_{jB}}{B_j - A_{jB}} \times \frac{A_j}{m_{stander}} 
\]

where:
- \(A_j\) — The net count rate of the all-energy peak of the i-th characteristic peak of the j-th nuclide in the tested sample, count/s;
- \(A_{jB}\) — The background count rate corresponding to \(A_j\), count/s;
- \(B_j\) — Net counting rate of the all-energy peak of the i-th characteristic peak of the j-th nuclide, count/s;
- \(B_{jB}\) — The background count rate corresponding to \(B_j\), count/s;
- \(A_{jB}^{\text{stander}}\) — Activity of standard source nuclide j, Bq;
- \(m_{\text{stander}}\) — Net mass of sample, kg.

3. Experiment

3.1. Materials and instruments

3.1.1. Materials
Ceramic tiles, 300*300.

3.1.2. Equipment
Soil monitoring efficiency calibration source, Chinese Academy of Metrology, No.TYH1807201;
High purity germanium gamma spectrometer, ORTEC Co., Ltd., GEM40-76;
Closed sample preparation crusher, Changsha Youxin Instrument Manufacturing Co., Ltd., YXZF/100A;
Electric blast drying oven, Shanghai Peiyin Experimental Instrument Co., Ltd., DHG-9070B;
Electronic balance, Shanghai Puchun Measuring Instrument Co., Ltd., JY5001.

3.2. Sample Preparation
2Kg ceramic tiles were crushed by a closed sample preparation crusher, ground and sieved (40-60 mesh). Place in an electric blast drying oven at 105 °C to dry to constant weight. Packed in \(\varphi 75 \times 70\)mm plastic box (consistent with standard source), compacted and flattened, sealed, to be tested.

3.3. Radioactive detection and limit standards
The specific activity of radionuclides \(^{226}\)Ra, \(^{232}\)Th, \(^{40}\)K was tested on the samples using a high-purity
germanium gamma spectrometer. Measure the background spectrum of the empty sample box, the soil standard source spectrum and the sample spectrum in sequence. The test spectrum is deducted the same background, and then count the energy peak position of the corresponding nuclide and branched nuclide. Record the net area and count error value of energy peaks. Calculate the specific activity values of $^{226}$Ra, $^{232}$Th and $^{40}$K according to the sample quality. Table 3 provides the Radioactivity information of the voluminal standard radioactive source.

| Nucleus | Weight/g | Activity (Bq) | Expanded uncertainty/% | Fixed value method |
|---------|----------|--------------|------------------------|-------------------|
| $^{226}$Ra | 338.52 | 233 | 5.1 | Standard solution + HPGe |
| $^{232}$Th | 790 | 645 | 7.0 | |
| $^{40}$K | | | 5.0 | |

3.4. Mathematical model for calculation of internal and external exposure index

According to GB 6566-2010[1], the internal exposure index model and the external exposure index model are:

$$I_{Ra} = \frac{C_{Ra}}{200} \quad (2)$$

$$I_{I} = \frac{C_{Ra}}{370} + \frac{C_{Th}}{260} + \frac{C_{K}}{4200} \quad (3)$$

$I_{Ra}$ — Internal exposure index;
$C_{Ra}$ — Specific radioactivity of natural radionuclide $^{226}$Ra in building materials, unit: Bq/kg;
$I_{I}$ — External exposure index;
$C_{Th}$ — Specific radioactivity of natural radionuclide $^{232}$Th in building materials, unit: Bq/kg;
$C_{K}$ — Specific radioactivity of natural radionuclide $^{40}$K in building materials, unit: Bq/kg;
200 is the $^{226}$Ra specific activity limit specified in the standard GB 6566-2010, unit: Bq/kg;
$370/260/4200$ — the specific activity limit values of $^{226}$Ra, $^{232}$Th, and $^{40}$K specified in the standard when each of them is present only when considering external exposure only, unit: Bq/kg.

4. Results and discussion

4.1. Analysis of radioactivity test results of the same sample at different equilibrium times

In order to study the changes of the specific activity of $^{226}$Ra, $^{232}$Th, and $^{40}$K in the samples of ceramic tiles under different equilibrium times, the same specifications and types of ceramic tiles produced by the same company were selected as the samples to be tested. Sealed 0-14d after preparation. The radionuclide analysis of the samples was carried out at the same test time (21600s) using a low background multichannel high purity germanium gamma spectrometer. $C_{Ra}$, $C_{Th}$, $C_{K}$ results show as follows.

| Decay time | $C^{226}$Ra (Bq/kg) | $C^{232}$Th (Bq/kg) | $C^{40}$K (Bq/kg) | $I_{Ra}$ | $I_{I}$ |
|------------|---------------------|---------------------|------------------|---------|--------|
| 0          | 86.91±6.74          | 105.21±4.29         | 830.47±5.01      | 0.43    | 0.84   |
| 1          | 84.08±7.03          | 106.11±4.26         | 887.17±4.79      | 0.42    | 0.85   |
| 2          | 84.22±6.97          | 108.07±4.25         | 880.24±4.83      | 0.42    | 0.85   |
| 3          | 82.94±7.13          | 109.13±4.25         | 892.25±4.78      | 0.41    | 0.86   |
| 4          | 81.09±7.24          | 108.70±4.22         | 901.22±4.69      | 0.41    | 0.85   |
| 5          | 81.06±7.28          | 108.56±4.20         | 917.96±4.69      | 0.41    | 0.85   |
| 6          | 80.75±7.29          | 109.39±4.23         | 925.67±4.70      | 0.40    | 0.86   |
| 7          | 80.79±7.28          | 109.11±4.21         | 918.21±4.68      | 0.40    | 0.86   |
| 10         | 80.09±7.28          | 110.56±4.20         | 920.86±4.69      | 0.40    | 0.86   |
It can be seen from the data in the table that the specific activity of ceramic tiles shows a stable trend with the extension of sealing time. From 0 to 7d, the specific activity of radionuclides varies greatly. In particular, in the case of testing immediately after sample preparation (unbalanced state). $C_{Ra}$ is the largest, mainly due to the the short-lived daughters of radionuclides are active. In the radioactivity test of ceramic tiles, the natural radionuclide radium 226$Ra$ first generates the gas radon 222$Rn$, and 222$Rn$ further decay to produce short-lived daughters 218$Po$, 214$Pb$, 214$Bi$, 214$Po$, etc. Each short-lived daughter is in an active state, breaking the decay balance, causing the test unstable results\[11-13\]. On 7--14d, the decay of 222$Rn$ and 222$Rn$ produced by the decay of radionuclide radium per unit time tends to be equal the. After 14d, the 226$Ra$ and 222$Rn$ radioactive decay tended to be balanced, and the test results at this time were the most stable. Therefore, we propose that the seal balance time is set to 14d to have the smallest effect on the test results, which can be used as a reasonable balance time as a test reference.

4.2. Analysis on the status of radioactive supervision and random inspection of ceramic tile products

Nan’an City, Fujian Province, is a famous hometown of stone and ceramics in the country. There are thousands of construction ceramic production enterprises in the area under its jurisdiction. In order to improve the product qualification rate of ceramic production enterprises within the jurisdiction and protect the personal health and safety of the citizens, the Municipal Market Supervision and Administration Bureau annually organizes special supervision and random inspection actions for the quality risk monitoring of ceramic tile products. Table 5 shows the specific radioactivity and the internal and external exposure index values of various ceramic tiles in Nan’an. The result shows that the specific activity of 226$Ra$ in various ceramic tiles ranges from 59.3 to 94.2 Bq/ kg, the specific activity of 232$Th$ ranges from 69.2 to 133.5 Bq/ kg, the specific activity of 40$K$ ranges from 441.5 to 826.4 Bq/ kg, and the internal exposure index $I_{Ra}$ ranges from 0.30 to 0.52, and the external exposure index $I_{T}$ ranges from 0.61 to 0.91, meet the requirement of $I_{Ra} \leq 1.0$, $I_{T} \leq 1.3$, meet the requirements of Class A product limits. Table 6 shows the radioactive qualification rate of ceramic tile products in Nan’an city from 2016 to 2020. The pass rate of the radionuclide project has been 100% in the past five years, indicating that the production enterprises within the jurisdiction can strictly control the radioactivity index of the product, and the radioactivity level exceeds zero. The result can eliminate the public's concern about the radiation of ceramic tile products to human radiation.

### Table 5. Specific activity & internal and external exposure index of various types of ceramic in Nan’an area.

| Types of ceramic tiles          | $C_{226}Ra$ (Bq/kg) | $C_{232}Th$ (Bq/kg) | $C_{40}K$ (Bq/kg) | $I_{Ra}$ | $I_{T}$ |
|--------------------------------|---------------------|---------------------|-------------------|---------|---------|
| Porcelain brick                | 70.5                | 92.1                | 787.3             | 0.37    | 0.73    |
| Square ceramic tiles           | 72.3                | 69.2                | 611.7             | 0.46    | 0.63    |
| Quartz ceramic tiles           | 70.0                | 92.3                | 787.7             | 0.42    | 0.73    |
| Ceramic tiles for interior walls| 64.3                | 83.0                | 600.2             | 0.31    | 0.64    |
| Ceramic tiles for exterior walls| 68.2                | 88.1                | 812.5             | 0.34    | 0.72    |
| Floor ceramic tiles            | 59.3                | 71.2                | 826.4             | 0.30    | 0.60    |
| Glazed ceramic tiles           | 72.3                | 69.2                | 611.4             | 0.41    | 0.62    |
| Unglazed ceramic tiles         | 66.4                | 94.2                | 441.5             | 0.33    | 0.61    |
| Nan’an Red Brick               | 94.2                | 133.5               | 583.2             | 0.52    | 0.91    |
Table 6. 2016-2020 supervision results of ceramic products in Nan'an city.

| Years | Product batch | Product percent of pass (%) | Radionuclide of Percent of pass (%) |
|-------|---------------|----------------------------|-----------------------------------|
| 2016  | 80            | 75                         | 100                               |
| 2017  | 75            | 80                         | 100                               |
| 2018  | 60            | 85                         | 100                               |
| 2019  | 65            | 85                         | 100                               |
| 2020  | 80            | 80                         | 100                               |

5. Conclusion

(1) The test results show that in the radioactivity test of ceramic tiles, the decay time is 14d, and the test results of the specific activities of each nuclide are the most stable, which can be used as the experimental basis for the detection workers.

(2) The data analysis of the monitoring results show that the radioactive level of ceramic tiles are within the safe and qualified range. Consumers should have a scientific attitude towards building material radiation without having to worry too much about the radioactivity of building ceramic products.

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