# Assessment of Environmental Safety Related Radioactivity Exposure in Zircon Sand

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## ABSTRACT

Zircon sand is one of major sources that are responsible for naturally occurring radionuclides in the earth's crust such as $^{238}U$ and $^{232}Th$. The mining and processing of zircon sand are found in several places in Indonesia such as in Bangka Belitung, Borneo and Riau. These activities are potential to produce some radioactivity exposure to the occupational area and surrounding environment. Therefore, the assessment of the environmental safety related radioactivity exposure in zircon sands is needed to ensure the safety of the worker and public. In this study, the concentration of uranium and thorium in zircon sands collected from several sites in Borneo were determined and evaluated using instrumental neutron activation analysis (INAA). Samples were irradiated in rabbit system facility of G.A Siwabessy, Serpong reactor with neutron flux ~ $10^{13}$ $n.cm^{-2}.s^{-1}$ for 15 minutes and 2 hours, and then counted with HPGe detector of gamma spectrometry. In order to assess the accuracy of the analysis, soil reference materials (RMs) were analyzed together with the samples. The results of reference material analysis showed a good agreement with the certificate value. The measurement results showed that the concentration of uranium and thorium varied widely depending on the sample origin. Uranium and thorium concentrations were 214.8 ± 101.7 and 209.9 ± 169.0 mg/kg, respectively. These values were equivalent to 2654 ± 1258 Bq/kg for $^{238}U$ and 848 ± 683 Bq/kg for $^{232}Th$, respectively. The results showed the annual equivalent dose average of 2.1 ± 1.04 mSv/year, which above the dose limit of the publis (1 mSv/year) and varies between 0.4 and 5.3 mSv/year. The characterization of zircon sands using INAA showed reliable results and could be utilized to assess the level of radioactive materials content in the zircon sands related to government regulation on zircon sand radioactive exposure, as well as the precaution to reduce needless exposure of the workers and public.

**Keywords**: NORM, TENORM, zircon sands, thorium, uranium, INAA

## INTRODUCTION

The exposure of human beings to ionizing radiation from natural sources is a continuing and inescapable feature of life on the earth. According to the United Nations Scientific Committee on Effect of Atomic Radiation report (UNSCEAR 2008), the greatest contributions to human exposure is from natural background radiation, and worldwide average annual effective dose per capita is 2.4 mSv [1,2]. Exploitation and processing of natural materials, minerals and other resources often increases naturally occurring radioactive concentrations material (NORM) in products, by-products, residues or waste arising from the industrial process. This process is often called TENORM (Technology Enhanced Natural Radioactive Materials) which has the potential to increase the radiation exposure to the workers and public [3,4]. Occupational exposure doses to workers are mostly measured, while the exposure doses to the public are usually assessed by indirect methods, typically using measurements performed in the environment or of environmental samples, modelling various exposure scenarios and employing data on population [1,5].

Several mining activities that have a potential high risk of radiation exposure have been regulated and make a big concern for regulation

body. Apart from uranium mining and milling, applications using natural radionuclides and, more recently, zircon industry and processing activities from raw materials zircon sand have generally not been fully evaluated from the perspective of public exposure [6]. Therefore, the assessment of the environmental safety related radioactivity exposure in zircon sands is needed to ensure the safety of the worker and public. In this study, the assessment of environmental safety through determination of radiation exposure and absorbed gamma dose rate as well as the external annual effective dose rate from zircon sands are carried out using neutron activation analysis.

Zircon sand is one of ore materials potential in Indonesia which one of its inventories located in several places i.e. Bangka Belitung, Borneo and Riau. In general, zircon sand ($ZrSiO_4$) contains other valuable mineral such as mineral rutile ($TiO_2$) and ilmenite ($FeTiO_2$), aluminium oxide, rare earth elements and naturally occurring radioactive materials (NORM) such as $U_3O_8$ and $ThO_2$ [4,6]. Characterization of zircon sands will enable and provide valuable information about the natural radioactivity elements to assess and evaluate the environmental safety related radiation exposure from zircon sands. A suitable, well established method of determination of radioactivity is using gamma spectrometry [7,8]. Other approaches using analysis method such as instrumental neutron activation analysis and particles induced X-ray emission have been conducted [9,10]. Nuclear analytical techniques neutron activation analysis is one of widely used methods for characterization of geological samples such as zircon sands. Instrumental neutron activation analysis (INAA) is a sensitive analytical technique useful for performing both qualitative and quantitative multi-element analysis of major, minor, and trace elements in samples from almost every field of scientific or technical interest [11]. It is one of the more mature analytical methods currently in uses and yet remains highly competitive with others in term of accuracy, detection limits and multi elemental capabilities.

## EXPERIMENTAL

### Materials and equipment

For this study, the materials used are vial polyethylene 0.3 mL, standard solution of uranium and thorium, mixed standard of radioactivity for detector calibration, and the equipment are flask, pipettes, semi micro balance and HPGe detector.

### Measurement of U and Th using INAA

Measurement using INAA was carried out in BATAN Bandung laboratory. INAA for products of neutron capture with medium half-lives was used to determine uranium, while for long lived products was used to determine thorium [9]. A total of 26 samples of zircon sands were collected from the mining sites in Borneo, then samples were dried under the sun and homogenized for analysis. Duplicate 25 mg portions were prepared for determination of short-lived products and triplicate 25 mg portions for long-lived INAA. The masses of each sample were recorded to ± 0.01 mg using an analytical balance. Synthetic standard solutions were prepared from metals or compounds of known purity solution. For validation and to assess the accuracy of the analysis, control samples of standard reference

materials SRM NIST 2711a Montana Soil, and International Atomic Energy Agency IAEA-Soil 7 were also analyzed in the same experimental conditions used in the sample analysis. Each sample, each RM and each standard were encapsulated in heat-sealed polyethylene vials prior to neutron irradiation. Samples were irradiated in rabbit system facility of G.A Siwabessy Serpong reactor of 15 MW with neutron flux ~$10^{13}$ n.cm$^{-2}$.s$^{-1}$. For determination of medium lived nuclides, each sample was irradiated for 15 minute together with standards and IAEA-RM, and then counted with HPGe detector of gamma spectrometry. The medium-lived assays were performed after decay times of 1-3 days. For INAA determination of longer-lived nuclides, samples, standards, control samples and IAEA RMs were placed into polyethylene irradiation containers and irradiated for 2 hours in the same facility in rabbit system facility of G.A Siwabessy Serpong reactor.

For determination long-lived nuclides were performed after approximately 2-4 weeks of decay, with each sample or element standard counted at a distance of 5-15 cm from the surface of gamma-ray germanium spectrometer. The measurement of U and Th were performed using Np and Pa, since after some decay time the whole U and Th will decay as Np and Pa [9]. Neutron irradiation into the samples cause the radionuclide $^{238}$U and $^{232}$Th activated as follow:

$$^{238}U + n \rightarrow {}^{239}U \rightarrow {}^{239}Np$$
$$^{232}Th + n \rightarrow {}^{233}Th \rightarrow {}^{233}Pa$$

Np was measured at 277.7 keV, while Pa was measured at 312 keV.

**Radiation hazard indices**

The mass concentrations of $^{238}$U and $^{232}$Th in the zircon sand can be converted into the activity concentrations assuming equilibrium exits in U and Th decay series, based on the formula [7,9]:

$$\acute{A} = \frac{C_{\acute{A}}.\lambda.\acute{I}.f_a}{W.C} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

where $A$ is the specific activity of the radioisotope (Bq/kg), $C_E$ is the elemental concentration (μg/g), $N$ is Avogadro's number ($6.02\times10^{23}$ atom/mol) and λ is decay constant $(s-1)$ of radionuclide, $f$ is the fractional atomic abundance of the radionuclide in nature (% or ppm), $W$ is the atomic mass (kg/mol) and $C$ is a constant (with value of 100 or $10^6$) that converts the ratio of the mass of the element to the mass of the sand into a percentage or parts per million (ppm). Activity levels are in Bq/kg with the formula (1) one can calculate that 1 ppb of $^{238}$U and $^{232}$Th corresponds to 12.34 and 4.05 Bq/kg, respectively [12,13].

The absorbed dose rates due to gamma radiations in air at 1 m above the ground surface for the uniform distribution of the naturally occurring radionuclides ($^{226}$Ra of U-series, $^{232}$Th and $^{40}$K) were calculated based on guidelines provided by UNSCEAR [1]. The conversion factors used to calculate the absorbed γ-dose rate ($D$) in air per unit activity concentration in Bq/kg (dry-weight) corresponds to 0.462 nGy/h for $^{238}$U, 0.604 nGy/h for $^{232}$Th and 0.0417 nGy/h for $^{40}$K.

$$D\ (\text{nGy/h}) = [0.462\ A(^{238}\text{U}) + 0.604\ A(^{232}\text{Th}) + 0.0417A(^{40}\text{K})]\ \text{nGy/h} \quad (2)$$

Table 1. Results of IAEA RM Soil and NIST 2711a

| Element | Analysis result (mg/kg) | Certificate value (mg/kg) | Bias (%) |
|---|---|---|---|
| IAEA RM soil | | | |
| Th | 8.18 | 8.2 | -0.2 |
| NIST 2711a | | | |
| Th | 15 ± 0.2 | 15 ± 1 | 0.0 |
| U | 3.07 ± 0.66 | 3.01 ± 0.12 | 2.0 |

where $A(^{238}U)$, $A(^{232}Th)$ and $A(^{40}K)$ are the activity concentrations of $^{238}U$, $^{232}Th$ and $^{40}K$, respectively.

## RESULT AND DISCUSSIONS

*Mass and radioactivity concentration of $^{238}U$ and $^{232}Th$ using INAA*

The analytical result of reference materials and standard with its certificate values are presented in Table 1. The results obtained were in good agreement with the certificate values and it showed a good recovery and precision.

The mass concentrations of uranium and thorium are shown in Figure 1, while the calculated activity levels in zircon sands are shown in Table 2. The results showed that

**Table 2.** Elemental and activity concentrations of radionuclides in the samples for mining sites

| Sample ID | $^{238}U$ | $^{232}Th$ |
|---|---|---|
| | Activity (Bq/kg) | Activity (Bq/kg) |
| A1 | 2390.8 ± 47.9 | 617.9 ± 11.3 |
| A2 | 883.9 ± 37.7 | 598.8 ± 4.3 |
| A3 | 3294.3 ± 39.1 | 858.5 ± 11.5 |
| A4 | 2415.4 ± 38.1 | 380.1 ± 10.7 |
| A5 | 1531.4 ± 62.4 | 473.8 ± 7.2 |
| A6 | 6181.8 ± 47.6 | 2419.0 ± 11.5 |
| A7 | 2768.5 ± 42.9 | 756.9 ± 11.1 |
| A8 | 1033.1 ± 54.6 | 472.2 ± 6.1 |
| A9 | 3616.2 ± 34.1 | 1198.1 ± 11.9 |
| A10 | 1563.8 ± 146.6 | 2479.2 ± 8.3 |
| A11 | 4221.2 ± 48.8 | 402.8 ± 10.9 |
| A12 | 1133.6 ± 73.5 | 454.3 ± 6.4 |
| A13 | 2250.1 ± 67.8 | 544.1 ± 10.8 |
| A14 | 353.4 ± 33.2 | 238.1 ± 9.5 |
| A15 | 3721.2 ± 52.7 | 551.9 ± 10.4 |
| A16 | 2780.6 ± 49.4 | 79.9 ± 3.1 |
| A17 | 2675.8 ± 49.6 | 1525.2 ± 11.9 |
| A18 | 2915.4 ± 52.8 | 2165.2 ± 12.6 |
| A19 | 2228.7 ± 46.2 | 621.0 ± 6.3 |
| A20 | 2629.0 ± 39.6 | 932.1 ± 6.4 |
| A21 | 2927.2 ± 43.2 | 409.2 ± 10.2 |
| A22 | 4579.2 ± 49.0 | 1961.4 ± 14.3 |
| A23 | 3679.6 ± 46.1 | 373.7 ± 11.8 |
| A24 | 2730.4 ± 47.4 | 631.2 ± 10.3 |
| A25 | 1745.0 ± 58.1 | 234.4 ± 6.0 |
| A26 | 2671.0 ± 58.0 | 728.7 ± 8.8 |

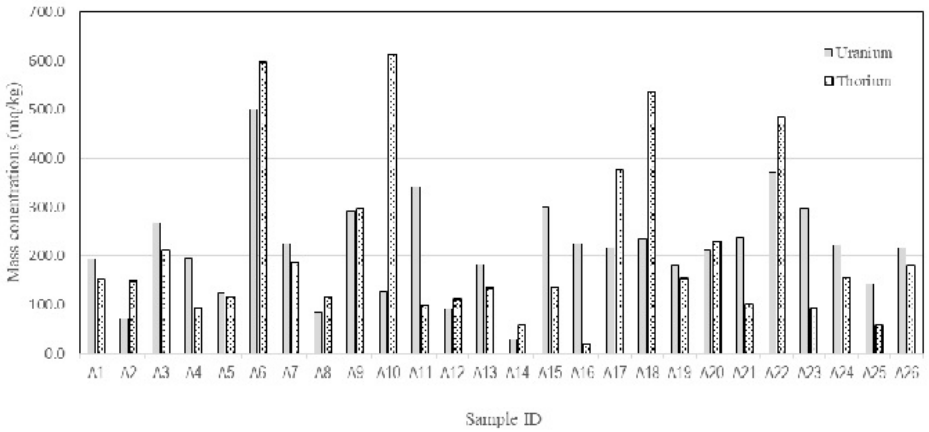


**Figure 1**. Mass concentration of U and Th in zircon sands

these radionuclides were significantly present in all samples. The mass concentration of U and Th were varied from 28.6 to 500.8 mg/kg and 19.7 to 612.1 mg/kg, respectively. Most of the samples about 85% are higher than 100 mg/kg, only several samples content lower concentrations. The average concentrations of uranium and thorium concentrations were 214.8±101.7 and 209.9±169.0 mg/kg, respectively. These values were equivalent to 2654±1258 Bq/kg for $^{238}$U and 848±683 Bq/kg for $^{232}$Th, respectively.

Syarbaini et al reported the average and ranges of activity concentrations of $^{238}$U and $^{232}$Th in soil collected from Bangka and Belitung islands were higher than the common areas world average of soil. Bangka and Belitung islands are geologically contains higher concentrations of natural radionuclides than most other areas. The mean activity concentrations of $^{238}$U and $^{232}$Th were 72.3 and 203 Bg/kg, respectively [14]. The current worldwide average values of $^{238}$U and $^{232}$Th are 37±4 and 33±3 Bq/kg, respectively [1]. Obviously $^{238}$U and $^{232}$Th in zircon sand in this study are higher than the worldwide soils and Bangka Belitung soil.

As the results in Table 2, most of the zircon sand samples produced total activity of $^{238}$U and $^{232}$Th with magnitude of more than 1000 Bq/kg. The IAEA basic security standard proposed that the materials should be regulated if the materials containing radionuclides of natural origin at activity concentrations above 1 Bq/g for radionuclides in the uranium and thorium decay series, and materials with radionuclides below 1 Bq/g could become regulated due to the existence of total activity limit [6]. Since the uranium series activity concentrations in zircon exceed 1 Bq/g, regulatory consideration is needed for the handling of these minerals, as well as their disposal as a result of their use.

Uranium and thorium are primarily associated with heavy minerals such as monazite, zircon and allanite [16–20]. Righi et al analyzed zircon sands used in a refractory plant, and they reported the mean radioactivity concentrations of $^{238}$U and $^{232}$Th in raw material zircon sands were 490 and 420 Bq/kg, respectively [18]. A review conducted by UNSCEAR on zircon sands reported the average activity concentrations are 3000 Bq/kg for $^{238}$U and 600 Bq/kg for $^{232}$Th [1]. Our results from this study were in similar

**Table 3.** Activity concentrations of $^{238}U$ and $^{232}Th$ in zircon sands from several countries

| Samples | $^{238}U$ (Bq/kg) | $^{232}Th$ (Bq/kg) |
|---|---|---|
| Zircon sand, India [8] | 3531 | 618 |
| Zircon sand, Orissa, India [12] | 3450±150 | 1850±180 |
| Zircon sand, Egypt [13] | 4910±160 | 1195±48 |
| Zircon sand, Australia [18] | 2400±200 | 520±40 |
| Zircon sand, South Africa [18] | 3200±300 | 520±40 |
| Zircon sand, Italy [18] | 2800±200 | 590±30 |
| Heavy sand, Kalatoli, Bangladesh [20] | 1651±133 | 2625±96 |
| Black sand, Egypt [13] | 260±25 | 410±43 |
| Monazite sand, Egypt [13] | 40580±1370 | 182425±9870 |
| Zircon sand, world average [1] | 3000 | 600 |
| Soil, world average [1] | 37 | 33 |
| Zircon sand, this study | 2654±1258 | 848±683 |

level of magnitude with those reported by UNSCEAR and other authors (Table 3). But these values are higher than soil and black/ iron sand and lower than monazite sand.

**Absorbed gamma dose rates and estimated annual effective dose**

From the activity concentrations of $^{238}U$ and $^{232}Th$ in zircon sands, the absorbed gamma dose rates in air were calculated. Based on other study reported that $^{40}K$ in zircon sand were less than 200 Bq/kg [8], and using the conversion factor of 0.0417 in formula (2) for $^{40}K$, we can calculate that $^{40}K$ contributes less than one hundredth. By assuming that $^{40}K$ contribution are less significant, the absorbed gamma dose rates in air from $^{238}U$ and $^{232}Th$ varied from 307 to 4317 nGy/ hour with average of 1738 nGy/hour. The conversion coefficient from absorbed gamma dose rate in air to effective dose (0.7 Sv/Gy) and outdoor occupancy factor (0.2) proposed by UNSCEAR (2008) were used to estimate the annual effective dose rates [1]. The annual effective dose received by population varies between 0.4 to 5.3 mSv/year. The results showed that more than 85% of the zircon sand samples contribute to the annual effective dose above the limit of 1 mSv/year and the average annual effective dose 2.1 mSv/year are higher than the permitted value.

However, it is evident that the annual effective dose received by a worker who handles zircon sand is likely to exceed 1 mSv with average 2.1 mSv. In such situations, the regulator could decide to impose radiation protection requirements. It is good practice in terms of occupational health and safety (OHS) and environmental protection to identify and implement any simple measures, for example limitation of occupancy periods near accumulations of material, wearing safety work devices (mask, hand gloves etc) and minimization of airborne dust, that may be effective in reducing the radiological impact on workers and members of the public.

## CONCLUSION

The measured radionuclides $^{238}U$ and $^{232}Th$ in the zircon sands showed higher radionuclide levels and higher activity concentrations than in soil or iron sand. Radiation exposure of workers in processing and mining of the zircon

sand is likely to occur at levels above the dose limit for members of the public (1 mSv/ year) and therefore radiation doses should be assessed as occupational exposures. The regulatory body must examine certain work processes to decide on the most appropriate regulatory. In some situations, authorization in the form of registration may be needed to ensure that certain basic control measures are maintained and implemented.

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