Technologically Enhanced Naturally Occurring Radioactive Materials (TENORM) Analysis of Bangka Tin Slag

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Abstract. Tin smelting industry in Bangka island has the potential to increase the concentration of TENORM (Technologically Enhanced Naturally Occurring Radioactive Materials) on the surface. The increase of TENORM in industrial waste i.e. tin slag 1, tin slag 2, tin slag 3 will have an impact on the workers and environment. In this research, concentration activity of TENORM in tin slag has been measured using gamma ray spectrometer HPGe detector. From the measurement result, the average concentration of Th-232 and U-238 series were higher than the limit proposed by United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR) 2000. The average of concentration activity of Th-232, Th-228, Ra-226, U-238 and K-40 are respectively 15.443 Bq/kg, 13.337 Bq/kg, 5017 Bq/kg, 6.289 Bq/kg, 8.253 Bq/kg. Radiological parameters such as Radium Equivalent Activity, External Hazard Indices, Absorption Dose and Effective Dose were calculated based on UNSCEAR 2000 report. In this research, Radiological parameters from tin slag are also higher than the maximum limit standard of UNSCEAR 2000. It means that the tin slag is hazardous materials and it will cause radiological effect to the workers.

Keywords: Tin Slag, TENORM, Concentration Activity, Radium Equivalent Activity, External Hazard Indices, Absorption Dose, Effective Dose

1. Introduction

The handling of radioactive waste from non-nuclear industries needs to be done well and safely. It aims to protect the public, workers and environment from the radioactive source and contamination effects. Therefore, natural radionuclide in radioactive waste must be identified both kinds of radionuclides and their concentration activity. Identifying kinds of radionuclide and their concentration activity is very important to know how the waste will be treated.

Cassiterite is the raw material in tin smelting industries. Its material consists of many kinds of impurities of minerals, such as monazite, ilmenite, rutile and topaz [1]. These materials, especially monazite contain some natural radionuclide such as thorium and uranium series [2].

Natural radionuclides such as the U-238, Th-232 and K-40 series can cause radiation exposure both externally and internally. External exposure could be caused by direct exposure of gamma particles. While, internal exposure occurs when the radioactive source enters the body through nose (breathing) or mouth (eating/drinking). Then, the radionuclides in the body will settle and accumulate in some parts of the body or organs and cause some damages to the body. For example, U-238 will accumulate in
lungs and kidneys, Th-232 will accumulate in lung, liver and bone tissue, while K-40 will precipitate and accumulate in muscle tissue [3].

Tin slag is a common waste material from smelting process of tin ore in tin industries. The first stage of tin ore smelting would produce slag 1, then melting process of slag 1 would produce slag 2 and melting process of slag 2 would produce slag 3. The slag 1 contains about 20-30\% of tin, the slag 2 contains about 20-3\% of tin and the slag 3 contains less than 3\% of tin [4]. The tin slag also contains many kinds of chemical compounds. The oxides concentration in the tin slag are shown in Table 1 below.

### Table 1. Initial Characterization of Bangka Tin Slag [4]

| Element | Concentration (%) |
|---------|-------------------|
| Ta$_2$O$_5$ | 0.33 |
| Nb$_2$O$_5$ | 0.64 |
| SiO$_2$ | 34.26 |
| CaO | 15.44 |
| TiO$_2$ | 11.92 |
| Al$_2$O$_3$ | 11.7 |
| Fe$_2$O$_3$ | 8.84 |
| ZrO$_2$ | 4.78 |
| Other Oxide | 12.06 |

Generally, natural radionuclide contains series of Th-232 and U-238. In addition, aside from containing oxide compounds, the tin slag also contains several types of natural radionuclides, especially Thorium and Uranium series carried from raw material.

In this paper, the concentration activity of natural radionuclide (U-238, Th-232, K-40) and their daughter products contained in tin slag have been estimated using gamma ray spectrometer HPGe detector. It is important to determine the level of activity of radionuclides in the tin slag to protect the public and workers. The radiological parameters of these radionuclide, such as Radium Equivalent Activity, External Hazard Indices, Absorption Dose and Effective Dose are also assessed and compared with the legal limit.

2. Material and Method

2.1. Sample

The samples in this research are taken from many areas of tin smelting factory. The samples consist of three kinds of tin slag (tin slag 1, tin slag 2, and tin slag 3). There are 30 samples in total, 10 samples (S1.1-S1.10) from tin slag 1 storage, 10 samples (S2.1-S2.10) from tin slag 2 storage and 10 samples (S3.1-S3.10) from tin slag 3 storage. These samples were crushed to get 100 mesh size (0.149 mm), weighed in ranges 200-300 gram, packaged into 200 ml vial and sealed. These samples are also stored for 30 days to get a balancing (at secular equilibrium between radium and its gaseous decay progenies) of decay of radionuclide [5].

2.2. Concentration Activity Measurement

In this research, concentration activity is generally measured based on International Atomic Energy Agency (IAEA) technical report series 295 and International Standard Organization (ISO) 10703: 2009. Then, gamma Spectrometer High Purity Germanium Detector (HPGeD) was used to obtain concentration activity of radioactive source in sample. The simple block diagram of HPGeD is shown in Fig 1 below.
Before doing measurement, calibration of energy and efficiency was needed to ensure accuracy and precision of measurement [7]. The background radiation due to the naturally occurring radionuclides in the environment around the detector was measured using an empty plastic container with the same sample's container shape and condition. After 30 days in storage, all samples are counted for 3600 second (1 hours) per sample. The spectrum data was evaluated and calculated using Eq. 1.

\[ C_{SP} = C_{avg} \pm U_T \]  

(1)

Where, \( C_{sp} \) is sample activity (Bq/kg), \( C_{avg} \) is average of activity (Bq/kg) and \( U_T \) is the uncertainty of measurement value (Bq/kg). Then, \( C_{avg} \) was obtained using Eq. 2.

\[ C_{AVG} = \frac{N_{SP} - N_{BG}}{\varepsilon_{\gamma} p_{\gamma} W_{sp}} \]  

(2)

Where, \( N_{SP} \) is sample counting rates (cps), \( N_{BG} \) is background counting rate (cps), \( \varepsilon_{\gamma} \) is counting efficiency (%), \( p_{\gamma} \) is gamma energy abundance (%), and \( W_{sp} \) mass of the sample (kg) [7].

3. Results and discussion

3.1. Concentration Activity

The measurement of concentration activity was found five radionuclides from series of Th-232, U-238 and K-40. The five radionuclides are (1) U-238 with minimum activity (1.500 ± 145,23) Bq/kg and maximum activity (13.856,95 ± 1.703,70) Bq/kg, (2) Ra-226 with minimum activity (3.098,10 ± 280,09) Bq/kg and maximum activity (7.720,00 ± 677,05) Bq/kg, (3) Th-232 with minimum activity (9.937,79 ± 943,31) Bq/kg and maximum activity (22.801,35 ± 2.152,86) Bq/kg, (4) Th-228 with minimum activity (8.991,28 ± 850,95) Bq/kg and maximum activity (21.110,09 ± 1.989,.53) Bq/kg, (5) K-40 with minimum activity (722,89 ± 102,02) Bq/kg and maximum activity (2.162,66 ± 235,93) Bq/kg. Distribution of radionuclides for 30 samples is shown in Fig. 2, Fig. 3, Fig. 4 below.
3.2. Radiological Parameter Assessment

3.2.1. Radium Equivalent Activity

To assess radiological effect from tin slag material, an index called Radium Equivalent activity (Ra\text{eq}) is calculated in this research. Ra\text{eq} is calculated by using Eq. 3.

\[
Ra_{eq} = A_{Ra} + 1.43A_{Th} + 0.077A_{K}
\]  

(3)

Where \(A_{Ra}\), \(A_{Th}\), \(A_{K}\) are concentration activity of Ra-226, Th-232, and K-40 in Bq.kg\(^{-1}\). Because distribution of natural radionuclide in sample of the tin slag is not uniform, Ra\text{eq} (Bq/kg) is calculated to show uniformity with respect to the exposure to radiation. Ra\text{eq} also compares to the specific activity of tin slag containing different concentration of U-238, Th-232 and K-40 [10], and it was assumed that gamma rate from 1 Bq/kg Ra-226 is equal with 0.7 Bq/kg Th-232 and 13 Bq/kg K-40 in this formula [8]. Ra\text{eq} in sample of Bangka tin slag is shown in Table 2 below.
Table 2. Radium Equivalent Activity in Tin Slag

| Range       | Radium Equivalent Activity (Bq/kg) |
|-------------|------------------------------------|
| Minimum     | 19.158,85                          |
| Maximum     | 39.852,20                          |
| Mean        | 27.084,00                          |

The maximum value of Ra\textsubscript{eq} in tin slag must be less than 370 Bq/kg. It is to keep external dose below 1 mSv/y [9]. From Table 2 above, it can be seen that Ra\textsubscript{eq} in tin slag is higher than 370 Bq/kg. It means that the tin slag is not safe to use.

3.2.2. External Hazard Indices

The external hazard indices (Hexs) is an evaluation of hazard of gamma radiation related to natural radioactive source. Hexs parameter should be below the unity (≤ 1) in order to keep external radiation dose less than 1 mSv/year [10]. Hexs in tin slag was calculated by using Eq.4.

$$\text{Hexs} = \frac{A_{Ra}}{370} + \frac{A_{Th}}{259} + \frac{A_{K}}{4810} \quad (4)$$

Where \(A_{Ra}\), \(A_{Th}\), \(A_{K}\) are concentration activity of Ra-226, Th-232, and K-40 in Bq.kg\(^{-1}\).

Table 3. External Hazard Indices in Tin Slag

| Range       | External Hazard Indices |
|-------------|-------------------------|
| Minimum     | 51,74                   |
| Maximum     | 107,62                  |
| Mean        | 73,14                   |

From Table 3 above, Hexs value in tin slag is higher than 1 (Hexs>1). It can be predicted that tin slag potentially causes exposure dose higher than 1 mSv/y.

3.2.3. Absorption Dose

Another way to assess radiological hazard and radiation exposure from natural radionuclide in tin slag aside Ra\textsubscript{eq} and Hexs is by calculating absorption dose (Dabs). Dabs is a direct connection between radioactivity concentration and exposure [10]. UNSCEAR 2000 report released that conversion factor connecting between radioactivity concentration on the ground and exposure rate in air at a distance 1 meter above the ground surface. Equation 5 has been used to calculate the absorption dose in this research.

$$\text{Dabs} = A \times Cf \quad (5)$$

Where, \(A\) is concentration activity (Bq/kg), \(Cf\) is conversion factor (nGy.h\(^{-1}\)/Bq.kg\(^{-1}\)). Cf for Th-232, U-238, and K-40 are respectively 0,662 nGy.h\(^{-1}\)/Bq.kg\(^{-1}\), 0,427 nGy.h\(^{-1}\)/Bq.kg\(^{-1}\) and 0,043 nGy.h\(^{-1}\)/Bq.kg\(^{-1}\) [9].

Table 4. Absorption Dose in the Air

| Range    | Dabs (nGy/h) |
|----------|--------------|
| Minimum  | 8631,41      |
| Maximum  | 21104,41     |
| Mean     | 12957,87     |
3.2.4. Annual Effective Dose Equivalent

In order to make an estimation of effective dose for the workers, the conversion factor 0.7 Sv.Gy\(^{-1}\) was used in this research. The conversion factor 0.7 Sv.Gy\(^{-1}\) has been recommended by UNSCEAR (1993,2000) report to estimate the effective dose that can be received by adults [11]. In this research, it was also used conversion factor 0.29 for outdoor occupancy factor in which assumed that workers in contamination area for 6-7 hours/day. The estimation of effective dose in unit mSv.year\(^{-1}\) is calculated by the following formula:

\[
E_{\text{eff}}(\text{mSv/year}) = D_{\text{abs}} \times 24(\text{hour}) \times 365(\text{day}) \times 0.29 \times 0.7 \times 10^{-6}
\]  

The estimation of effective dose that was received by workers due to tin slag in this research is shown in Table 5 below:

| Range       | Estimation of Effective Dose (mSv.year\(^{-1}\)) |
|-------------|-----------------------------------------------|
| Minimum     | 15.35                                         |
| Maximum     | 37.53                                         |
| Mean        | 23.04                                         |

4. Conclusion

From this research, it has been known that Bangka tin slag contains natural radionuclide dominated by Th-232 series and U-238 series. Concentration activity of Th-232 series and its progeny (Th-228) is higher than U-238 series and its progeny. More than 60 % of mean of total activity is given by Th-232 series and its progeny Th-228.

Furthermore, radiological parameter estimation shows that Ra\(_{eq}\) in tin slag is higher than 370 Bq/kg. It means that tin slag is hazardous and not safe to use. Generally, Bangka tin slag potentially can cause external exposure more than 1 mSv/y. Estimation of absorption dose in the air shows high value about 12957.87 nGy/h and the workers may accept a highly effective dose about 23.04 mSv/y. This value is higher than maximum limit recommended by UNSCEAR 2000.

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