RADIATION HAZARD OF SOLID METALLIC TAILINGS IN SHANGLUO, CHINA

by

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The radiation hazards of five kinds of different solid metallic tailings collected from Shangluo, China were determined on the basis of natural radioactivity measurements using low background multichannel gamma ray spectrometry. The activity concentration of ^{226}Ra, ^{232}Th and ^{40}K in the tailings ranged from 5.1 to 204.3, 3.8 to 28.5, and 289.6 to 762.3 Bq/kg, respectively. The radium equivalent activities and the external hazard indexes of all studied metallic tailings were below the internationally accepted value of 370 Bq/kg and unity, respectively. The internal hazard index of vanadium tailings exceeded unity, while the internal hazard indexes of other analyzed metallic tailings were less than unity. The indoor air absorbed dose rate values for all studied metallic tailings except lead-zinc tailings and gold tailings were higher than the world population-weighted average of 84 nGy/h and the annual effective dose values of all metallic tailings except for vanadium tailings were lower than 1 mSv. The study showed that vanadium tailings present a radiation hazard and their usage as building materials should be restricted.

Key words: metallic tailing, building material, natural radioactivity, radiation hazard, radium equivalent activity

INTRODUCTION

Metallic tailings are the residues from the extraction of metal from the crushed and ground ores. The effluent and tailings from the mill are discharged as slurry to a waste-retention pond for disposal. When the ores are of a low grade, the majority of the tonnages of ores processed at the mill is disposed as tailings. Metal mineral resources are abundant in Shangluo of the Shaanxi province, China, so after processing, plenty of metallic tailings are produced every year in Shangluo and stored in tailings reservoirs. Such underutilization of the metallic tailings not only places a heavy economic burden of waste management on the mining industry, but also brings about severe environmental problems and ecological risks in the mining regions [1-3]. Metallic tailings can pollute soil due to dust emissions resulting from surface erosion [4-6] and can contaminate water due to the leaching of heavy metals or radioactive metals [7-9]. Mine drainage is the main source and transfer pathway of radionuclides to plants [10-13] and even pollutes the diet near the mining and milling tailings region [14-16].

Using tailings to produce building materials not only can realize zero-emission of tailings wastes, but also could offer a new raw material for the building industry. Construction materials produced from metallic tailings can be used as a substitute for conventional building materials with the benefits of farmland conservation, environmental protection and energy saving [17]. Nowadays, more and more metallic tailings are used to produce construction materials, such as engineered cementitious composites [18], mortar [19], concrete [20, 21], bricks [22-27], *etc*. However, these kinds of building materials can pose radiation risks to residents. Therefore, it is necessary to determine the natural radioactivity level of metallic tailings when they are used as building materials. Determining the radioactivity of metallic tailings is important for the assessment of population exposure to radiation. Furthermore, the knowledge of this radioactivity can help to set the standards and national guidelines for the use and management of such metallic tailings and assess the associated radiation hazard to the people. To our knowledge, the natural radioactivity of Shangluo metallic tailings has not been investigated. The aims of

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this study are to investigate the activity concentration of natural radionuclides in the main metallic tailings of Shangluo and evaluate the associated radiation hazards to individuals by using a radium equivalent activity, external and internal hazard indexes, indoor air absorbed dose rate and annual effective dose. Results would provide basic information for the safe use and management of metallic tailings.

MATERIALS AND METHODS

Samples

Five types of tailings of metal from the mining plant in Shangluo of northwestern China, *i. e.*, molybdenum tailings (MoT), vanadium tailings (VT), gold tailings (AuT), iron tailings (FeT), and lead-zinc tailings (PbZnT), were investigated. Four to six samples of each type of the investigated metallic tailings were collected from the local tailings ponds and about 1 kg tailings were collected for each sample. All samples were crushed and milled to pass through a 1 mm mesh, then homogenized and dried in an oven at 105 °C until they reached a constant mass. The prepared samples were weighed and hermetically sealed in radon impermeable polyethylene containers (7.0 cm height and 6.5 cm diameter) and stored for 4 weeks to ensure that radium, thorium, and their short-lived progenies were in the secular equilibrium [28].

Radioactivity measurement

A 3 × 3 in. NaI(Tl) gamma ray spectrometric system with >8 % energy resolution (^{137}Cs 661.6 keV) was used to determine the concentrations of natural radionuclides ^{226}Ra, ^{232}Th, and ^{40}K in the investigated metallic tailings. The detector, housed in a cylindrical shield with a thickness of 10.5 cm and a height of 38 cm, was coupled to a 1024 microcomputer multi-channel pulse height analyzer and the system was calibrated for the γ-energy range 50 keV to 3.2 MeV. Activity concentrations were averaged from photopeaks measured at several γ-ray energies. For ^{226}Ra, the 609.3 and 1764.5 keV gamma lines, emitted from ^{214}Bi, were used. For ^{232}Th, the gamma lines of ^{212}Pb and ^{208}Tl at 238.6 and 2614 keV, respectively, were averaged. ^{40}K was measured directly through its gamma photopeak at 1460.8 keV.

The standard sources for ^{226}Ra and ^{232}Th (in a secular equilibrium with ^{228}Th) were prepared by mixing the known activity contents with the matrix material of phthalic acid powder. Analar grade potassium chloride (KCl) of a known amount of the same geometry was used as the standard source of ^{40}K. Sealed cylindrical polyethylene containers were used to keep the prepared standard sources. So the loss of gaseous daughter products of ^{226}Ra and ^{232}Th which may lead to disturbance in the radioactive equilibrium can be avoided. Each sample was counted for 18 000 s and counted two times before an average was calculated [28].

Calculation of radiation hazard parameters

The radium equivalent activity (Ra$_{eq}$), the external hazard index (H_{ex}), the internal hazard index (H_{in}), the indoor air absorbed dose rate (D), and the annual effective dose (AED) were calculated for all investigated metallic tailings to assess the associated radiation hazards using the equations [29-31]

$$\mathrm{Ra}_{eq} = C_{Ra} + 1.43 C_{Th} + 0.077 C_K \tag{1}$$

$$H_{ex} = \frac{C_{Ra}}{370} + \frac{C_{Th}}{259} + \frac{C_K}{4810} \tag{2}$$

$$H_{in} = \frac{C_{Ra}}{185} + \frac{C_{Th}}{259} + \frac{C_K}{4810} \tag{3}$$

$$D = 0.92 C_{Ra} + 1.1 C_{Th} + 0.08 C_K \tag{4}$$

$$AED = D \times 8760 \times 0.8 \times 0.7 \times 10^{-6} \tag{5}$$

where C_{Ra}, C_{Th}, and C_K are the activity concentration of ^{226}Ra, ^{232}Th, and ^{40}K in Bq/kg, respectively, 0.8 is the indoor occupancy factor, and 0.7 is the conversion coefficient (Sv/Gy) from the absorbed dose in air to the effective dose received by an individual.

RESULTS AND DISCUSSION

Specific activity

The range and mean value of ^{226}Ra, ^{232}Th, and ^{40}K concentration in the investigated metallic tailings are shown in tab. 1. The activity concentrations of

Table 1. Activity concentration [Bqkg^{-1}] of ^{226}Ra, ^{232}Th, and ^{40}K in metallic tailings of Shangluo, China

Tailings	^{226}Ra		^{232}Th		^{40}K		Total activity	
	Range	Mean	Range	Mean	Range	Mean	Range	Mean
MoT	53.6-61.2	57.4	9.5-12.2	10.9	519.8-538.7	529.3	593.2-601.8	597.5
VT	182.7-204.3	193.4	8.5-11.6	10.0	415.9-551.5	466.6	631.4-742.8	670.0
AuT	15.5-15.9	15.7	20.3-28.5	24.4	516.3-561.1	538.7	560.7-596.9	578.8
FeT	16.6-31.7	23.9	9.3-17.9	13.6	716.9-762.3	737.7	751.2-802.3	775.2
PbZnT	5.1-5.3	5.2	3.8-4.2	4.0	289.6-304.3	297.0	298.5-313.8	306.2

Table 2. The calculated value of the radiological hazard index in metallic tailings of Shangluo, China

Tailings	Statistics	Ra_{eq} [Bqkg^{-1}]	H_{ex}	H_{in}	D [nGyh^{-1}]	*AED* [mSv]
MoT	Min	108.7	0.294	0.439	102.9	0.505
	Max	118.7	0.321	0.486	111.3	0.546
	Mean	113.7	0.307	0.462	107.1	0.525
VT	Min	232.2	0.628	1.121	216.2	1.060
	Max	252.6	0.683	1.235	233.8	1.147
	Mean	243.7	0.658	1.181	226.3	1.110
AuT	Min	87.7	0.237	0.297	81.4	0.399
	Max	96.4	0.260	0.303	87.2	0.428
	Mean	92.0	0.248	0.291	84.3	0.414
FeT	Min	97.1	0.262	0.307	92.1	0.452
	Max	102.7	0.277	0.363	99.5	0.488
	Mean	100.2	0.271	0.335	96.0	0.471
PbZnT	Min	32.8	0.088	0.108	32.0	0.157
	Max	34.6	0.094	0.102	33.8	0.166
	Mean	33.7	0.091	0.105	32.9	0.161

^{226}Ra, ^{232}Th and ^{40}K in the metallic tailings ranged from 5.1 to 204.3, 3.8 to 28.5, and 289.6 to 762.3 Bq/kg, respectively. The ^{226}Ra concentrations were higher than the ^{232}Th concentrations in all tailings, molybdenum (MoT), vanadium (VT), iron (FeT), and lead-zinc (PbZnT), except in gold tailings (AuT) where the ^{232}Th concentration is higher than the ^{226}Ra concentration. ^{40}K accounts for 69.6 % to 97.0 % of the total activity concentration, *i. e*., it is the largest contributor to the total activity concentration for all tailings samples. Larger diversity of the natural radioactivity level was found among five different metallic tailings (tab. 1). The lowest activity concentrations of ^{226}Ra, ^{232}Th, and ^{40}K were found in PbZnT and all values were lower than the worldwide population-weighted average value for soils (32, 45, and 420 Bq/kg for ^{226}Ra, ^{232}Th, and ^{40}K, respectively, [31]). The mean ^{226}Ra concentrations of MoT and VT are relatively high when compared to the worldwide population-weighted average value for soil, while the mean ^{226}Ra concentrations of AuT and FeT are lower than the average value of worldwide soil. The mean activity concentrations of ^{232}Th in all investigated samples of tailings were lower than the worldwide population-weighted average value for soil [31]. The mean ^{232}Th concentration is highest in AuT, while values for MoT, VT, and FeT are very similar. The mean concentrations of ^{40}K in all investigated metallic tailings except for PbZnT were higher than the worldwide population-weighted average value for soil [31].

Radiation hazard of metallic tailings

The radiation hazard arising from the use of metallic tailings in the construction of dwellings was calculated using equations given in the previous section and the results are presented in tab. 2. The highest Ra_{eq} value of 252.6 Bq/kg was found in VT, but all Ra_{eq} values were lower than the recommended limit of 370 Bq/kg for building materials [31]. The calculated values of H_{ex} for the metallic tailings are well below unity ranging from 0.088 in PbZnT to 0.683 in VT, while the H_{in} values exceed unity only for VT samples (tab. 2). The relative contributions of ^{226}Ra, ^{232}Th, and ^{40}K to H_{in} for all investigated metallic tailings were estimated and the results are shown in fig. 1. ^{226}Ra is the largest contributor to H_{in} in VT (88 %) and these high ^{226}Ra activity concentrations imply a high release of ^{222}Rn, which can enter the human body through inhalation and can cause internal radiation exposure through Rn and its short-lived decay products. The estimated D values for the investigated metallic tailings range from 32.0 nGy/h in PbZnT to 233.8 nGy/h in VT. The D values of MT, VT, and FeT are significantly higher than the world population-weighted average indoor absorbed gamma dose rate of 84 nGy/h [31], while the D values of PbZnT and AuT are lower than and close to the world population-weighted average indoor absorbed gamma dose rate, respectively. The calculated values of *AED* due to gamma ray emission from ^{226}Ra, ^{232}Th, and ^{40}K in the studied metallic tailings range from 0.157 mSv in PbZnT to 1.147 mSv in VT (tab. 2). All investigated metallic tailings except for VT have the *AED* values lower than the recommended limit of 1 mSv for building materials [30]. The higher *AED* values for VT samples are mainly due to the contribution of the higher ^{226}Ra concentration in the samples, which contributes about 79 % to *AED* (fig. 2).

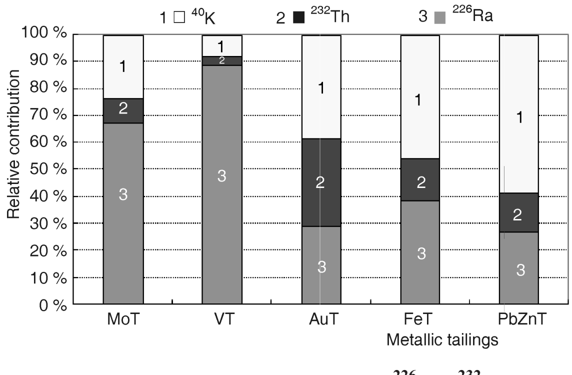

Figure 1. The relative contribution of ^{226}Ra, ^{232}Th, and ^{40}K to H_{in} in metallic tailings

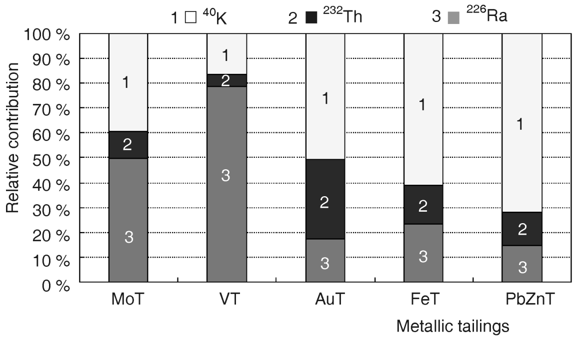

Figure 2. The relative contribution of ^{226}Ra, ^{232}Th, and ^{40}K to *D* and AED in metallic tailings

CONCLUSIONS

Natural radioactivity levels and radiation hazards of various tailings (molybdenum, vanadium, gold, iron, and lead-zinc) collected from Shangluo, China, were determined in the present study. Different types of metallic tailings have diverse natural radioactivity levels. Vanadium tailings from Shangluo have a high ^{226}Ra concentration, which can cause an internal radiation and annual effective dose to individuals above internationally accepted limits. Consequently, the use of these tailings in the construction of dwellings should be restricted, whereas other investigated metallic tailings in Shangluo can be safely used as building materials and do not pose any significant source of radiation hazard. These study results provide the basic data of natural radioactivity for the investigated metallic tailings. In addition, when local building materials enterprises use vanadium tailings to produce other building materials such as brick and concrete, *etc*., the additive amount of vanadium tailings should be noted and the natural radioactivity of the products should be monitored.

AUTHORS' CONTRIBUTIONS

All metallic tailings samples were collected by S. Zhuang, J. Li, and Q. Li. Activity measurements of samples were carried out by S. Zhuang under supervision and guidelines of X. Lu. All authors discussed the results. The manuscript was written by S. Zhuang and reviewed by X. Lu. The figures were prepared by S. Zhuang and X. Lu.

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Сукаи ЖУАНГ, Ксинвеи ЛУ, Џиантао ЛИ, Киан ЛИ

РАДИЈАЦИОНИ РИЗИК ОД МЕТАЛНИХ ОТПАДАКА У ЧВРСТОМ СТАЊУ У ШАНГЛУОУ У КИНИ

На основу мерења природне радиоактивности нискофонским вишеканалним гама спектрометром утврђен је радијациони ризик пет врста металних отпадака у чврстом стању сакупљених у Шанглуоу у Кини. Концентрације активности ^{226}Ra, ^{232}Th и ^{40}K у отпацима биле су у опсезима: 5.1-204.3, 3.8-28.5 и 289.6-762.3 Bq/kg, респективно. Активности еквивалента радијума и индекси спољашњег ризика свих испитаних металних отпадака, испод су међународно прихваћених вредности од 370 Bq/kg и јединице, респективно. Индекс унутрашњег ризика отпадака ванадијума прелази јединичну вредност, док су индекси унутрашњег ризика осталих испитаних металних отпадака испод јединице. Вредности јачина апсорбованих доза испитаних металних отпадака, у ваздуху у затвореним просторијама, повећане су у односу на светски просек са тежинским фактором популације од 84 nGy/h, осим за отпатке олово-цинка и злата, а годишње ефективне дозе свих металних отпадака су испод 1 mSv, осим за ванадијум. Истраживање показује да отпаци ванадијума представљају радијациони ризик те његову примену у грађевинском материјалу треба забранити.

Кључне речи: метални отпадак, природна радиоактивност, радијациони ризик, активност еквивалента радијума