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Determination of naturally occurring radioactive materials (NORMs) in metallic minerals and related industry in Kosovo

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Abstract: In this study, we present the preliminary results on the identification of Naturally Occurring Radioactive Materials (NORMs) in minerals, products, and residue streams coming from Pb-Zn and Fe-Ni industries in Kosovo. The activity concentrations of ^{40}K, ^{226}Ra and ^{232}Th in 21 samples are determined by using gamma-ray spectrometry method with HPGe detectors. The activity concentration of ^{40}K, ^{226}Ra and ^{232}Th is found to be 123±9 Bq/kg, 9±1 Bq/kg and 6±1 Bq/kg in Pb-Zn minerals, and 4±2 Bq/kg, 8±1 Bq/kg and 2±1 Bq/kg in Fe-Ni minerals. In general, we observe an increase of radionuclides in tailing and slag residues. However, according to the Council Directive No. 2013/59/EURATOM, the NORM concentrations in industrial residues from stream processes are much lower than the exemption reference levels for ^{238}U, ^{232}Th and ^{40}K, respectively 1 kBq/kg, 1 kBq/kg and 10 kBq/kg. Therefore, these residues do not pose any radiological hazard due to their management and further disposal. Regarding the radiological hazard, these residues are studied for the possibility of recycling them as building materials and further investigations of the physical-mechanical and chemical properties need to be undertaken.

Keywords: Natural radioactivity; NORM; Metallic minerals; Gamma-ray spectrometry; Radiological hazard

INTRODUCTION

According to the 2012 to 2025 exploration strategy[1], the lead-zinc and iron-nickel mining and processing industry constitutes an important mining sector in Kosovo. The lead-zinc deposits lie in the northeastern part of the Republic of Kosovo, mainly in the "Trepça metalogenic belt" with the main occurrences in Stantërg complex, Crnac-Bellobërd complex and Hajvali-Badovc-Artana complex[2]. Ferronikeli Smelter Complex located near Drenas, in central Kosovo, treats ores from Kosovo in Gllavica mine and imported from Albania, Philippines and Indonesia. From the geological point of view Gllavica deposit is located in the south east near Ultrabasic Massif of Golesh, part of the geotectonic area of Vardar[3] .

According to the Council Directive no. 2013/59/EURATOM[4] of the EU, the miming of ores and lead smelting are defined as an industrial sector, which potentially could lead to the concentration of NORM. Indeed, materials containing radionuclides of natural origin and being subject to regulation because of their radioactivity are known as Naturally Occurring Radioactive Material (NORM). The most important sources of natural radioactivity are due to the presence of ^{238}U, ^{232}Th and ^{40}K in the Earth.

This preliminary study aims the identification and characterization of natural radioactive materials "NORM" in metallic minerals and related industry, in order to prepare for the industrial sector to the consequences of the implementation of Council Directive no. 2013/59/EURATOM[4] of the EU. Indeed, there is a lack of information regarding the NORM concentrations in Pb-Zn industry, where only few studies report data like, Poland [5]. While, to our knowledge, there is no data on Fe-Ni industry. Therefore, the objective of this study focuses the characterization of natural activity concentration of ^{40}K, ^{238}U and ^{232}Th decay present in raw materials and industrial residues. These data will be used to evaluate the strategies of waste management and reuse. Moreover, these preliminary results are expected to serve as a foundation for guiding the strategy and planning of the detailed evaluation of the metallic mineral mining sector of the Republic of Kosovo.

MATERIAL AND METHODS

Sample collection and preparation: The materials that potentially concentrate the natural radioactivity as a result of industrial processes, and which are of interest to this study are collected directly on the site (**Figure 1).** Generally, three types of samples are identified (21 samples in total): mineral ores of Pb-Zn and Fe-Ni, intermediate product (Pb and Zn concentrate) and industrial residues (Artana and Kishnica Pb-Zn tailings and Fe-Ni electrical furnace and converter slag).

Figure 1: Approximate location of the mineral ore extraction sites and related industries.

Samples are homogenized to a grain size of less than 2 mm and dried for at least 24 h at a temperature of 105°C until a constant weight was achieved. Therefore, samples were then transferred into cylindrical polycarbonate boxes of 180 cm^3 volume and sealed hermetically. Sealed samples were left undisturbed for at least four weeks prior to being measured by the HPGe gamma spectrometer to establish a radioactive equilibrium in the ^{226}Ra decay chain segment.

Gamma-ray spectrometry measurements: Samples were measured using the high-resolution gamma-ray spectrometry technique. The fully automated spectrometer consists of two 60% relative efficiency coaxial p-type HPGe gamma-ray detectors, with an energy[6] resolution of ~1.9 keV at 1332.5 keV (^{60}Co) . The absolute full energy peak efficiency of the MCA_Rad is calibrated using certified reference materials of natural origin [7]. The overall uncertainty in the efficiency calibration is estimated to be less than 5%.

The ^{226}Ra activity concentration was determined by analyzing the two main gamma emissions of radon progenies, ^{214}Pb (at 352 keV) and 214Bi (at 609 keV), and calculating the weighted average. ^{228}Ra was determined through its direct progeny, ^{228}Ac gamma emissions (at 338 keV and 911 keV). While, ^{228}Th activity concentration was determined by analyzing the two main gamma emissions of radon progenies, ^{212}Pb (at 239 keV) and ^{208}Tl (at 583 keV). Instead, the activity concentration of ^{40}K was determined from its only gamma emission at 1460 keV.

RESULTS AND DISCUSSION

Activity concentration: The activity concentrations of ^{40}K, ^{226}Ra and ^{232}Th (at 1σ standard deviation) are summarized in **Table 1.** The average activity concentration of ^{40}K in Pb-Zn mineral ore is found to be 123±9 Bq/kg, which show a clear depletion in Pb and Zn concentrates, respectively 13±1 Bq/kg and 15±2 Bq/kg. This evidence indicates the potassium is present in lesser content in Pb-Zn mineralization. As a consequence of tailings mass reduction exhibit a higher concentration of ^{40}K, from 202±12 to 343±22 Bq/kg, respectively in Artana and Kishnica. The rounded average activity concentration of ^{226}Ra and ^{232}Th in Pb-Zn mineral ore is found to be respectively 9±1 Bq/kg and 6±1 Bq/kg. The rounded average activity concentrations of ^{226}Ra in Pb and Zn concentrates are respectively 8±1 Bq/kg and 5±1 Bq/kg, while the rounded average activity concentrations of ^{232}Th are respectively 7±1 Bq/kg and 4±1 Bq/kg. These values show for ^{226}Ra and ^{232}Th a comparable activity concentration in Pb concentrate and a slight depletion in Zn concentrate. This may be either due to affinity of ^{226}Ra and ^{232}Th with Pb mineralization or due to the separation in the cyclic process. The tailing residues exhibit a higher concentration of ^{226}Ra and ^{232}Th respectively, 18±1 Bq/kg and 10±5 Bq/kg.

Table 1: The average activity concentration of natural radionuclides of ^{40}K, ^{214}Pb, ^{214}Bi, ^{228}Ac, ^{208}Tl in Bq/kg and the associated uncertainty (k = 1).

Sample ID		**^{40}K ± σ (Bg/kg)**	**^{238}U-series**		**^{232}Th-series**	
			^{214}Pb ± σ (Bg/kg)	**^{214}Bi ± σ (Bg/kg)**	**^{228}Ac ± σ (Bg/kg)**	**^{208}Tl ± σ (Bg/kg)**
Pb-Zn industry	Pb-Zn mineral ore	123 ± 9	8.8 ± 0.7	9.1 ± 1.0	6.4 ± 0.7	6.4 ± 0.8
	Pb concentrate	13 ± 1	7.0 ± 0.5	9.1 ± 0.8	6.8 ± 1.1	6.5 ± 0.6
	Zn concentrate	15 ± 2	5.5 ± 0.5	5.3 ± 0.6	3.7 ± 0.5	3.7 ± 0.6
	Tailing (Artana)	202 ± 12	18.9 ± 1.2	17.5 ± 1.5	5.2 ± 0.8	5.5 ± 1.6
	Tailing (Kishnica)	343 ± 22	17.1 ± 1.2	16.5 ± 1.5	14.2 ± 1.2	15.3 ± 1.2
Fe-Ni industry	Fe-Ni mineral ore	4 ± 2	8.1 ± 1.1	7.9 ± 1.4	2.4 ± 0.7	2.0 ± 1.9
	Slag – electric furnace	19 ± 4	7.9 ± 2.2	7.4 ± 1.7	5.0 ± 0.9	5.2 ± 1.2
	Slag - converter	12 ± 3	6.6 ± 0.9	6.5 ± 0.9	4.6 ± 0.9	4.5 ± 0.9

Few studies on the activity concentration of natural activity in Pb-Zn industry report maximum activity concentrations of ^{40}K, ^{226}Ra and ^{228}Ra in mineral ore[5] respectively 65 Bq/kg, 21 Bq/kg and 17 Bq/kg and in tailing 194 Bq/kg, 40 Bq/kg and 17 Bq/kg. These results show a general tendency of increase of radioactivity in tailings, however the activity concentrations are found to be relatively low.

The average activity concentration of ^{40}K in Fe-Ni mineral ore is found to be 4±2 Bq/kg, which show a clear increase in electric furnaces and converter slags, respectively 19±4 Bq/kg and 12±3 Bq/kg. The rounded average activity concentration of ^{226}Ra and ^{232}Th in Fe-Ni mineral ore is found to be respectively 8±1 Bq/kg and 2±1 Bq/kg. The converter slag residues exhibit a slightly higher activity concentration of ^{226}Ra respect to electric furnace slag, respectively 8±2 Bq/kg and 7±1 Bq/kg. However, the activity concentration of ^{226}Ra in slag residues is comparable to the activity concentration of the mineral ore. While, the activity concentration of ^{232}Th is generally higher in slag residues, respectively 5±1 Bq/kg for both electrical furnace and converter slag. This evidence may be related to the refractory properties of thorium.

Residue management and assessment of radiological hazard: In accordance with Article 24 of Council Directive 2013/59/EURATOM[4] reference levels of radioactivity concentration of artificial and natural radionuclides are provided in Annex VII. The reference levels of activity concentration of natural radionuclides are 1 kBq/kg ^{238}U, 1 kBq/kg ^{232}Th and 10 kBq/kg ^{40}K, which can be used for allowing the reusing of solid materials, recycling, conventional disposal (conventional landfill) or burning them. As we discussed above, there is an increase of NORM in residues. However, activity concentrations of ^{238}U, ^{232}Th and ^{40}K in tailings (industrial residues) are much smaller than the reference levels.

According to the Council Directive 2013/59/EURATOM[4], the reference level applying to indoor external exposure to gamma radiation emitted by building materials, in addition to outdoor external exposure, shall not exceed 1 mSv/y. The radiological hazards due to building materials can be conservatively investigated by assessing the activity concentration index (ACI) according to the following equation:

$$ACI = A_{226Ra}/300 + A_{232Th}/200 + A_{40K}/3000 \leq 1$$

Where A_{226Ra}, A_{232Th} and A_{40K} are the measured activity concentrations in Bq/kg for radium, thorium and potassium, respectively. The activity concentration index applies to building materials and in the case of constituent materials like cements; an appropriate mixing factor needs to be applied.

Based on the calculation of the index of the concentration of activity, (ACI < 1), we conclude that tailing and slag residues do not cause the exceeding of the gamma radiation reference dose level (1 mSv/y) as defined in Article 75 of this Directive. Consequently, the solid materials (tailings) can be reused or recycled as construction materials (if filling the physical-mechanical) without showing significant radiological risk.

CONCLUSION

The average activity concentrations of ^{238}U, ^{232}Th and ^{40}K in Pb-Zn mineral ore are found to be 9±1 Bq/kg, 6±1 Bq/kg and 123±9 Bq/kg respectively. From these results, it is observed a depletion of activity concentration of ^{40}K in Pb and Zn concentrates. On the other hand, the activity concentrations of ^{226}Ra and ^{232}Th are found to be comparable in Pb concentrate while a slight depletion is observed in Zn concentrates. In general, tailings show an increase of activity concentration of ^{238}U, ^{232}Th and ^{40}K respectively 18±1 Bq/kg, 10±5 Bq/kg and 272±82 Bq/kg.

The average activity concentrations of ^{238}U, ^{232}Th and ^{40}K in Fe-Ni mineral ore are found to be 8±1 Bq/kg, 2±1 Bq/kg and 4±2 Bq/kg respectively. From these results, it is observed a comparable activity concentration of ^{226}Ra in electric furnaces and converter slag. On the other hand, the activity concentration of ^{232}Th is generally higher in slag residues, probably due to the refractory properties of thorium.

However, the activity concentrations of ^{238}U, ^{232}Th and ^{40}K in tailings and slags (industrial residues) are much smaller than the reference levels, respectively 1 kBq/kg, 1 kBq/kg and 10 kBq/kg. Based on these results according to the Council Directive no. 2013/59/EURATOM, the solid materials (tailings) can be conventionally damped (managed in conventional landfill). Also, based on the calculation of the index of the concentration of activity, ACI <1, we conclude that tailing and slag residues not cause exceeding the reference gamma radiation dose of (1 mSv/y). Consequently, the solid materials (tailing and slags) can be reused or recycled as construction materials (if filling the physical-mechanical) without showing significant radiological risk.

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