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EVALUATION OF RADIOACTIVITY IN THE PHOSPHOGYPSUM STOCKPILE OF “HIV” VELES, THE REPUBLIC OF NORTH MACEDONIA

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Abstract:The production of phosphoric acid from natural phosphate ore generates an industrial waste product named phosphogypsum. Phosphogypsum contains considerable amounts of natural radionuclides from the ^{238}U chain, originating from the ore but enriched during the technological process. In order to perform radiological characterization of the “HIV” (Chemical Industry Veles) phosphogypsum stockpile, five phosphogypsum samples were collected and analyzed. The mean values of gross alpha and beta specific activities ± standard deviation values were: (950±104) Bq/kg and (1694±220) Bq/kg, respectively. Further analysis showed increased gross activities of radionuclides of the ^{238}U chain, while the radionuclides of the ^{232}Th chain and ^{40}K were below the detection limit. The mean values of the specific activities of ^{238}U and ^{226}Ra were (360±55) Bq/kg and (280±84) Bq/kg, respectively. The estimated annual outdoor effective dose, at 1m received by adults was 0.25 mSv/y, which is below a dose limit of 1 mSv/y for members of general public. The results obtained in this study show that radionuclides, although present in relatively high concentrations in the phosphogypsum pile, do not imply an increased external radiation risk for members of the population. The possible use of phosphogypsum in civil construction and agriculture may not be excluded if conditions of prior good planning taking into account the radionuclides activities exist.

Keywords: Phosphogypsum, Radioactivity, ^{238}U chain.

1. INTRODUCTION

The population of the Earth is constantly exposed to various types of ionizing radiation. By origin, the sources of ionizing radiation are divided into natural and artificial. Exposure to artificial sources is a result of their application in: medicine (diagnostics and therapy), industry, or from radionuclides present in the environment as a result of nuclear tests and the Chernobyl nuclear disaster in the previous century. Based on a number of studies, it was proven that the largest contribution to the total exposure of the population comes from nature. Cosmic and terrestrial radiation belong to the group of natural sources. The dose that a person receives during one year of outdoor cosmic radiation is generally constant for a given space (depending on altitude) and is much lower compared to the dose originating from terrestrial radioactivity [1].

The radioactive isotopes of the ^{238}U and ^{232}Th chains, as well as ^{40}K, present in all terrestrial materials are the major sources of human exposure. By their origin, they are defined as naturally occurring radioactive materials: NORM. In the case where naturally occurring radioactive material is subjected to a technological process in which radioactive isotope interference occurs, it is categorized as technologically enhanced naturally occurring radioactive material: TENORM. The contents of radionuclides in soil and rock (NORM) vary depending on their origin (geology), while their contents in TENORM depend on both the geological origin and the technological process itself.

Phosphogypsum is a waste product in the fertilizer industry, generated in the process of producing phosphoric acid from the phosphate ore [2,3]. It contains natural radionuclides from the ^{238}U and ^{232}Th chains as well as ^{40}K originating from the phosphorous ore but with a disrupted ratio due to the technological process itself [4]. The deposited phosphogypsum, characterized by increased radionuclide concentrations of the ^{238}U chain, causes

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environmental contamination: soil, water and atmosphere [5]. For these reasons, among others, it is necessary to also make a radiation characterization of landfills, i.e. to assess the possible adverse effects on the environment and on people directly [6,3].

Accordingly, the idea appeared to make a radiation characterization of the deposited phosphogypsum from the “HIV” (Chemical Industry Veles) factory, situated in the central part of Republic of North Macedonia. During its operation, from 1979 to 2003, $3.7x10^6$ t gypsum on $70x10^3$ m² (≈53 t/ m²) were deposited 1.5 km southwest of the factory complex near the village of Zgropolci (Figure 1). This paper presents the measured results of the TENOM radionuclides specific activities in phosphogypsum sampled from the stockpile and external risk assessment.

Figure 1. Position of the stockpile

2. MATERIAL AND METHODS

Five phosphogypsum samples were collected at a depth of 50 cm from the pile (Figure 2) and sent to “Activation laboratories” in Canada for analysis.

After the standard samples preparation, the radionuclides content was measured in them. The measurements of: gross alpha and beta activities, ^{40}K as well as the radionuclides from the ^{238}U and ^{232}Th chains were done. The results were expressed as specific activities (activity per unit dry mass) in Bq/kg.

Figure 2. Phosphogypsum sampling in the field

3. RESULTS

Table 1 shows the results of the measured specific activities in the five samples as well the basic descriptive statistics is in the Table 2.

The results indicate that gross alpha and beta activities were measured in all samples and that they mainly originate from the isotopes of the ^{238}U chain. Specific ^{40}K activities and the isotopes of the ^{232}Th chain were below the detection level. Variations between the gross alpha and beta activities, as well as the activities of ^{238}U in the five samples ranged from 11% to 15% and were lower compared to the ^{226}R variations of 30%.

Table 1. Measured specific activities in 5 phosphogypsum samples from the "HIV" stockpile

Sample number	Gross α (Bq/kg)	Gross β (Bq/kg)	^{40}K (Bq/kg)	^{232}Th (Bq/kg)	^{238}U (Bq/kg)	^{226}Ra (Bq/kg)
1	1090	1610	<1000	<10	300	200
2	980	1740	<1000	<10	400	300
3	980	1980	<1000	<10	400	400
4	820	1380	<1000	<10	300	200
5	880	1760	<1000	<10	400	300

Table 2. Basic descriptive statistics of the specific radioactivity in the samples

	Gross α (Bq/kg)	Gross β (Bq/kg)	^{238}U (Bq/kg)	^{226}Ra (Bq/kg)
Arithmetic mean	950	1694	360	280
Minimum	820	1380	300	200
Maximum	1090	1980	400	400
Standard deviation	104	220	55	84
Coefficient of variation	11%	13%	15%	30%

Higher values of the measured specific activities than the natural ones were substantiated by comparing them with the results published by the previous studies in the Republic of North Macedonia. The mean values of the measured gross alpha and beta specific activities in the phosphogypsum are higher than the corresponding mean activities published for soils sampled in the vicinity of Veles [7] (Figure 3a). The activities of ^{238}U are higher than the values obtained for the soils in Veles [7] and higher than the average values for all of Macedonia[8], (Figure 3b).

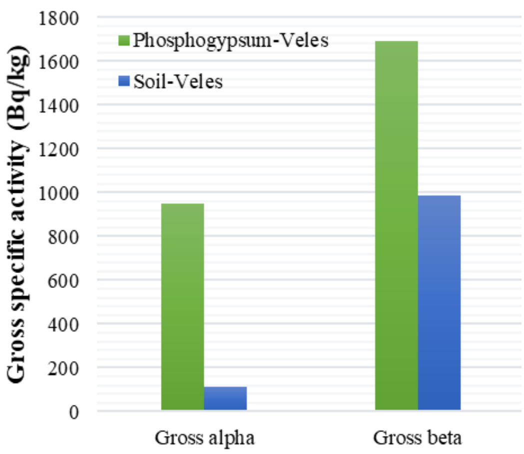

Figure 3a. Comparison between gross alpha and beta specific activities in the phosphogypsum and soil of Veles [7]

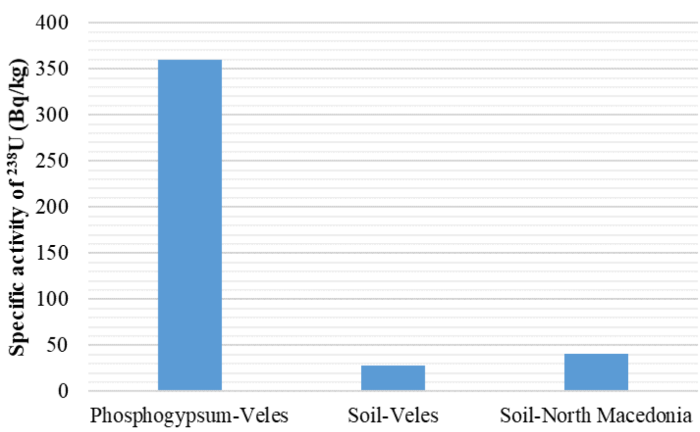

Figure 3b. Comparison between ^{238}U specific activities in the phosphogypsum and soil of Veles [7] *and soil in North Macedonia*

There are a number of studies in literature that examined the content of radionuclides in phosphogypsum as well as its application. Overall, as in this study, the specific activities of ^{232}Th and ^{40}K are lower than the values of ^{238}U chain radionuclides. On the other hand, the published activities of ^{226}Ra are generally higher than those of ^{238}U, which is not the case in our study. Figure 4 shows the values of specific activities of ^{226}Ra in the phosphogypsum from some countries compared to the average value of ^{226}Ra in this study. The values of ^{226}Ra in the phosphogypsum from Egypt [9], Croatia [10], Jordan [11], Slovenia [12], Spain [13], Greece [3], Serbia [14]are higher compared to the results of this study.

In accordance with the data in literature (for example references: [15-16], further application of the phosphogypsum in construction and agriculture is not excluded.

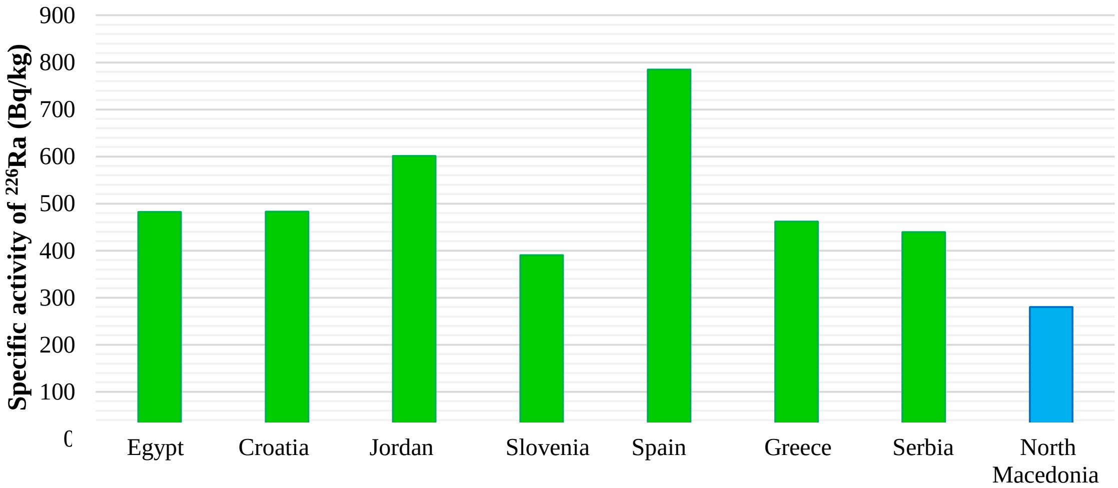

Figure 4. Comparison of the results of specific activities of ^{226}Ra in phosphogypsum from North Macedonia with results published by other countries

The estimation of the annual effective dose for individuals of the population was based on the UNSCEAR methodology [13].The dose rate *D* (Gy/h) at a height of 1 m is first estimated based on the specific activities of ^{40}K, ^{232}Th, and ^{238}U, using the following equation:

$$D = 0{,}462(^{238}\text{U})+0{,}604(^{232}\text{Th})+0{,}0417(^{40}\text{K}), \quad (1)$$

where for ^{238}U the arithmetic mean of all samples was used, and for ^{40}K and ^{232}Th the corresponding limits of detection were considered.

The obtained value for *D* (Gy/h) was then used to estimate the annual effective dose D_E (Sv/y)[1], according to the equation:

$$D_E = D \cdot 0{,}7 \cdot 8760 \cdot 0{,}2 \quad (2)$$

where: 0.7 (Sv/Gy) is the conversion factor, 1 y = 8760 h and 0.2 is the outdoor occupancy factor.

Accordingly, the estimated annual effective dose to be received by individuals from the population staying at the stockpile 0.2 of time during one year is 0.25 mSv/y.

Although the estimate was based on the worst-case scenario, the estimated D_E is still lower than the dose limit of 1 mSv/y for individuals from the population.

4. CONCLUSION

In this study, based on the measurement of specific activities of the radionuclides in the samples of phosphogypsum, sampled from the HIV Veles stockpile, the following results were obtained:

- The gross alpha and beta specific activities in the stockpile are higher than their values in the soils from Veles and the surrounding area;
- The specific activities of ^{40}K and radionuclides of the ^{232}Th chain were below the detection level. The presence of ^{238}U and ^{226}Ra with activities higher than the soil activities has been identified;
- The arithmetic mean value of the specific activity of ^{226}Ra in this study is lower than the values reported in such studies conducted in other countries;
- Based on the estimated dose made under the worst-case scenario, no increased external radiation risk from the stockpile has been identified for individuals from the population.

Further research on the effects of the stockpile on the environment is recommended. On the basis of a large number of scientific studies published in relevant literature, the application of phosphogypsum in construction and in agriculture is possible.

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ОЦЕНА РАДИОАКТИВНОСТИ У СТОГУ ФОСФОГИПСА "ХИВ" ВЕЛЕС, РЕПУБЛИКА СЕВЕРНА МАКЕДОНИЈА

Сажетак: Производњом фосфорне киселине из природне фосфатне руде ствара се индустријски отпадни производ назван фосфогипс. Фосфогипс садржи знатне количине природних радионуклида из ланца ^{238}U, који потичу из руде, али се обогаћују током технолошког процеса. Да би се извршила радиолошка карактеризација фосфогипса, "ХИВ", (хемијске индустрије Велес), анализирано је пет узорака фосфогипса. Средње вредности укупне алфа и бета специфичне активности ± вредности стандардне девијације биле су: (950 ± 104) Bq/kg и (1694 ± 220) Bq/kg, респективно. Даља анализа радионуклида показала је да повећане укупне активности потичу од радионуклида из ланца ^{238}U, док су радионуклиди ланца ^{232}Tk и ^{40}K испод границе детекције. Средње вредности специфичних активности од ^{238}U и ^{226}Ra биле су

(360 ± 55) Bq/kg и (280 ± 84) Bq/kg, респективно. Процењена годишња ефективна доза на отвореном, на 1 m, за одрасле, била је 0,25 mSv/y, што је испод ограничења дозе од 1 mSv/y за појединце. Резултати добијени овом студијом показују да радионуклиди, иако присутни у релативно високим концентрацијама у фосфогипсном стогу, не увећавају радијациони ризик од екстерног зрачења за појединце популације. Могућа употреба фосфогипса у грађевинарству и пољопривреди није искључена, само у условима претходног доброг планирања узимајући у обзир активности радионуклида.

Кључне речи: фосфогипс, радиоактивност, ланац ^{238}U.

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