

## CHARACTERIZATION OF PHOSPHOGYPSUM FROM DUMPS OF VELES PHOSPHATE FERTILIZER FACTORY (NORTH MACEDONIA) AND ENVIRONMENTAL IMPLICATIONS

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**Abstract:** The work of the factory for the production of fertilizers in the area of Veles (Republic of North Macedonia) resulted in a residual amount of approximately 3.4 million tons of phosphogypsum, which was deposited at the dump adjacent to the plant between 1980 and 2003. So far, no remediation of the phosphogypsum dump has been performed. This paper presents the results obtained from representative samples taken from the phosphogypsum dump by applying the following methods: analytical methods (ICP-MS, FUS-ICP-MS), mineralogical methods, X-ray powder diffraction (powder-XRD), electron microscopy (SEM-EDS), and high-resolution  $\gamma$ -ray spectrometry. The samples contain crystalline gypsum (Ca-sulphate), Fe-hydroxide, Ba-sulphate, Ca-fluoride, Si-oxy-hydroxide and zircon. The gross alpha specific activities varied between 820 Bq/kg and 1090 Bq/kg with an average of  $950 \pm 104$  Bq/kg, while the gross beta specific activities ranged from 1380 Bq/kg to 1980 Bq/kg with an average of  $1694 \pm 220$  Bq/kg.

**Key words:** phosphogypsum; fertilizer; mineralogical; alpha and beta specific activities

### INTRODUCTION

Phosphogypsum is obtained in the phosphoric acid obtaining process by treating phosphate rock (phosphorites) with sulfuric acid (Al Hwaiti et al., 2015; Al Masri et al., 2004; Bituh et al., 2009; Mesić et al., 2016; Degirmenci et al., 2007). The fertilizer plant "Chemical Industry Veles" (abbreviated as HIV) is a factory for the production of fertilizers near the village of Zgropolci in the immediate vicinity of the river of Vardar, central N. Macedonia. The factory is located about 12 km southeast of the city of Veles and about 15 km from the lead and zinc smelter "MHK Zletovo" (Figure 1).

The plant for phosphoric acid within the "Chemical Industry Veles" was first opened in 1979. In February of the following year the production of monoammonium phosphate (MAP) began and the plant for the production of fertilizers was opened in May 1980. The factory ceased operations in June 2003.

The factory was primarily built to use the sulfuric acid obtained in the metallurgical complex of the lead and zinc smelter "MHK Zletovo" near

Veles. The main production of the plant was the production of phosphoric acid, the production of monoammonium phosphate and the production of fertilizers. The capacity for the production of phosphoric acid was projected at 50,000 tons with a dihydrate procedure, and the maximum realized capacity was 33,000 tons per year.

The factory represents an ecological hot spot in the surrounding area due to the unorganized acid waste waters discharge and the gypsum dump, which has been in use since the plant started operation in 1979 until its closure in 2003.

There are 3.7 million tons of gypsum on the gypsum dump and it covers 70.000 m<sup>2</sup>. The gypsum dump is located about 1.5 km southwest of the factory complex in a small valley between hills (Dimitrioski, 2011).

The gypsum dump was filled by a pipeline, whereby the solid waste materials were transported in the form of a phosphogypsum suspension. Beside this dump, the factory also completely polluted the river of Vardar through the discharge of waste waters.



**Fig. 1.** Landscape of dump of the Veles fertilizer factory

## MATERIALS AND METHODS

Twenty samples of phosphogypsum were taken from the dump in the vicinity of the factory HIV-Veles during August 2018 (Figure 2). The samples were taken by digging wells with a depth of 1 m, and 2 kg of each sample was taken from the bottom of the well. The samples were dried at a temperature of 105°C, packaged in plastic bags and

delivered to the Activation Laboratories Ltd. in Canada. Chemical and geochemical composition tests were performed on the delivered samples using the Fusion-ICP and ICP-MS methods. Radioactivity tests were performed using the methods of gross alpha, gross beta, gamma scan, and uranium equilibrium.



**Fig. 2.** Process of taking of samples on the dumps

Quantitative tests of the mineral composition were performed using the method of quantitative X-ray diffraction analysis and tests were performed on the composition of the present mineral phases applying SEM-EDS.

#### *Fusion – ICP*

Samples were prepared and analyzed in a batch system. Each batch contains a method reagent blank, certified reference material and 17% replicates. Samples were mixed with a flux of lithium metaborate and lithium tetraborate and fused in an induction furnace. The molten melt was immediately poured into a solution of 5% nitric acid containing an internal standard and mixed continuously until completely dissolved (~30 minutes). The samples were run for major oxides and selected trace elements on a combination simultaneous/sequential Thermo Jarrell-Ash ENVIRO II ICP or a Varian Vista 735 ICP. Calibration was performed using seven prepared USGS and CANMET certified reference materials. One of the seven standards was used during the analysis for every group of 10 samples.

#### *ICP-MS*

Fused samples were diluted and analyzed by Perkin Elmer Sciex ELAN 6000, 6100 or 9000 ICP-MS. Three blanks and five controls (three before the sample group and two after) were analyzed per group of samples. Duplicates were fused and

analyzed every 15 samples. Instruments were recalibrated every 40 samples.

#### *Gross alpha. Gross beta*

Approximately 0.1 g of a dry and homogeneous sample mass was transferred into a Planchet and spread evenly with few drops of methanol before counting in Protean ICP 650 Internal Proportional Detector Automatic Low-Level Alpha/Beta Counter.

#### *Gamma scan*

A dry and homogeneous sample mass was determined and put into a standard geometry for gamma counting. The samples were counted for long enough to meet the required sensitivity of measurement. The multi-channel analyzer performed a Pulse Height Analysis to store the isotope counts from the sample according to the produced energy. The Canberra Genie-2K V3.2 software locates and analyzes the peaks, subtracts background, identifies the nuclides and corrects parent/daughter interferences. A report is generated and activity is calculated in Bq/g.

#### *Uranium equilibrium*

A dry and homogeneous sample mass was determined and put into a standard geometry for gamma spectroscopy analysis. The samples were sealed and stored for a minimum of 28 days before

analysis.  $U^{238}$  and  $Th^{232}$  were determined by gamma spectrometry from daughter products of the uranium and thorium series ( $Pb^{214}$  &  $Bi^{214}$  for  $U^{238}$  and  $Pb^{212}$  &  $Ac^{228}$  for  $Th^{232}$ ). The method assumes that the decay series are in radioactive equilibrium. The Canberra Genie-2K V3.2 software locates and analyzes the peaks, subtracts background, identifies the nuclides and corrects for parent/daughter interferences. A report is generated and activity is calculated in Bq/g.

#### *Quantitative X-ray diffraction analysis*

20 samples were submitted for quantitative X-ray diffraction analysis. Each powdered sample was mixed with corundum and loaded into a standard holder. Corundum was added as an internal standard. The X-ray diffraction analysis was performed on a Panalytical X'Pert Pro diffractometer, equipped with a Cu X-ray source and an X'Celerator detector, operating at the following X-ray conditions: voltage 40 kV; current 40 mA; range 5–70 deg  $2\theta$ ; step size

0.017 deg  $2\theta$ ; time per step 50.165 seconds; divergence slit – fixed angle  $0.5^\circ$ . The crystalline mineral phases were identified in X'Pert High Score Plus using the PDF-4 Minerals ICDD database. The quantities of the crystalline minerals were determined using the Rietveld method. The Rietveld method is based on the calculation of the full diffraction pattern from crystal structure data.

#### *SEM-EDS*

A representative portion of each sample was split using the micro-Riffle splitter. Two grams of the sample was embedded in the epoxy resin for preparing round polished sections. The samples were received prepared and no further preparation on the samples was performed at Actlabs-Canada.

The analysis was performed by FEI MLA 650F using manual methods with EDX detectors. The Field Emission Gun was used at an accelerating voltage of 25 kV and a spot size of 6 with a working distance of 13 mm.

## RESULTS AND DISCUSSION

### *Chemical characterization*

#### *Major element and impurities concentrations*

Table 1 presents the results of the chemical testing of phosphogypsum from the dump of HIV Veles obtained by the Fused ICP method.

From the presented results we can conclude that the content of the main elements in the phosphogypsum from the dump of HIV Veles is very close to the content of the main elements in phosphogypsum from Algeria, Tunisia, Morocco, Brazil, Egypt and Turkey (Table 2) (El Zrelli et al., 2018). It should be mentioned that only the concentration of CaO in the phosphogypsum from HIV Veles is lower than the cited sites in Table 2. From the aspect of the presence of impurities in the phosphogypsum from the dump of HIV Veles, the concentration of  $SiO_2$  (Table 1) should be mentioned as being relatively high compared to the cited samples of phosphogypsum from other sites (Table 2). Here the concentration of  $SiO_2$  has a mean value of 8.22% – a relatively high value for such materials. This comes as a consequence of surface decomposition processes of phosphogypsum (Reguigui et al., 2005) and the extraction of CaO in surface waters. It should also be mentioned that the small differences existing in the concentrations of the main

elements in the phosphogypsum from the dump of HIV Veles (Table 1) and the concentrations of the main elements in phosphogypsum from other countries (Table 2) can be explained by different mineral compositions as well (Al Masri et al., 2004).

Table 1

*Chemical composition of the phosphogypsum from the Veles dump (N. Macedonia) FUS-ICP method (%)*

	Average	Median	Min	Max	SD
$SiO_2$	8.22	8.41	2.88	15.62	3.52
$Al_2O_3$	0.12	0.10	0.06	0.25	0.06
$Fe_2O_3$	0.09	0.085	0.04	0.2	0.04
MnO	0.004	0.0035	0.003	0.006	0.001
MgO	<0.01	<0.01	<0.01	0.01	0.000
CaO	28.87	29.77	24.09	32.44	2.73
$Na_2O$	0.06	0.05	0.04	0.10	0.02
$K_2O$	<0.01	<0.01	<0.01	0.04	0.02
$TiO_2$	0.01	0.010	0.006	0.037	0.01
$P_2O_5$	0.48	0.48	0.32	0.55	0.05
LOI	19.83	19.885	16.60	21.09	1.04
F	0.40	0.365	0.26	0.63	0.11

Table 2

Concentrations (% weight) of major elements in phosphogypsum samples from Veles (N. Macedonia) and other regions (El Zrelli et al., 2018)

Elements	Tunisia <sup>a</sup>	Morocco <sup>b</sup>	Algeria <sup>c</sup>	Egypt <sup>d</sup>	Turkey <sup>e</sup>	Brazil <sup>f</sup>	Macedonia <sup>g</sup>
CaO	32.80	38.14	31.18	32.13	32.04	37.05	28.8
P <sub>2</sub> O <sub>5</sub>	1.69	0.69	0.87	1.82	0.50	nd	0.47
SiO <sub>2</sub>	1.37	0.86	0.88	8.78	3.44	1.39	8.22
SO <sub>2</sub>	44.4	48.12	40.90	37.60	44.67	nd	41.7
Al <sub>2</sub> O <sub>3</sub>	0.11	0.19	0.10	0.29	0.88	0.14	0.12
Na <sub>2</sub> O	nd	0.17	1.32	nd	0.13	nd	0.05
Fe <sub>2</sub> O <sub>3</sub>	0.03	0.21	0.03	0.35	0.32	0.89	0.08
MgO	0.01	nd	0.06	0.09	Nd	0.30	0.01
K <sub>2</sub> O	nd	0.01	nd	nd	Nd	nd	0.02
F	0.55	nd	1.20	0.80	0.79	0.20	0.40

nd – not determined; <sup>a</sup>El Taher et al., 2007; <sup>b</sup>Renteria-Villalobos et al., 2010; <sup>c</sup>Kacimi et al, 2006; <sup>d</sup>Değirmenci and Okucu, 2007; <sup>e</sup>Da Conceição and Bonotto, 2006; <sup>f</sup>Present study

#### Trace elements concentrations

The concentrations of trace elements and rare earth elements (REE) were determined in all samples taken (20 samples) and the results are shown in Table 3.

From the results shown, it can be stated that in the phosphogypsum samples from the dump of HIV Veles the concentration of trace elements is very similar to the concentration in the phosphogypsum from Tunisia (Table 4) (El Zrelli et al., 2018).

Table 3

Concentrations of the microelements and REE in phosphogypsum from the Veles dump (N. Macedonia) (in ppm) FUS-ICP-MS method

	Average	Median	Min	Max	SD		Average	Median	Min	Max	SD
Zn	40.00	40.00	30.00	80.00	15.81	Dy	3.54	2.85	1.98	8.19	1.93
Sr	683.75	731.50	316.00	832.00	148.66	Ho	0.74	0.63	0.44	1.56	0.33
Y	39.65	36.55	24.50	67.60	10.37	Er	2.11	1.86	1.28	4.03	0.78
Zr	15.50	12.00	2.00	52.00	12.19	Tm	0.26	0.24	0.17	0.47	0.08
Nb	0.43	0.45	0.20	0.60	0.17	Yb	1.45	1.35	1.05	2.23	0.31
Ba	168.50	187.50	37.00	253.00	58.61	Lu	0.19	0.19	0.16	0.24	0.02
La	24.51	18.45	11.90	59.30	14.20	Hf	0.39	0.30	0.20	1.20	0.26
Ce	33.54	16.85	10.80	129.00	36.98	Ta	0.02	0.02	0.02	0.03	0.00
Pr	4.72	2.95	2.01	15.40	4.06	W	2.19	1.10	0.50	10.10	3.22
Nd	19.35	12.35	8.73	61.00	16.40	Tl	0.16	0.10	0.06	0.66	0.15
Sm	3.72	2.49	1.75	11.40	3.05	Pb	19.08	13.00	6.00	87.00	21.81
Eu	0.95	0.66	0.40	2.78	0.71	Th	0.76	0.64	0.31	1.89	0.44
Gd	3.79	2.78	2.08	10.20	2.52	U	2.63	1.65	0.32	10.40	2.62
Tb	0.59	0.46	0.32	1.50	0.36						

Table 4

*Concentrations (ppm) of trace elements in phosphogypsum samples  
from North Macedonia and other country*

Trace elements	Tunisia <sup>a</sup>	Morocco <sup>b</sup>	Brazil <sup>c</sup>	North Macedonia <sup>d</sup>
Zn	137	8	7.5	40
Cu	9.6	21	4	9
Cr	13	20	2.5	18
Pb	0.90	6.2	11.5	19
As	1	–	–	4
Ag	0.44	–	–	0.6
Be	0.05	–	–	0.1
Mn	3	–	–	2
Bi	0.02	–	–	0.1
Co	0.3	–	0.93	0.2
Cs	0.05	–	–	0.05
Ga	0.87	1	–	0.75
Ge	0.17	–	–	0.2
Tl	0.38	–	–	0.15
Hf	0.10	–	5.6	0.38
In	0.005	–	–	0.05
Mo	1.86	–	–	1.56
Nb	0.80	1	–	0.42
Ni	4.10	1	4	15
Rb	0.60	2	–	0.5
Sb	0.09	–	–	0.9
Sn	0.20	–	–	0.25
Ta	0.07	–	4.3	0.02
V	3	4.7	–	3
W	0.2	–	–	2.18
Zr	2.6	6.2	10	15.5
Y	53.2	144	–	39.6
La	46.3	86	100	24.51
Ce	74.4	–	200	33.54
Sc	0.2	–	–	0.2
Th	0.74	–	43	0.75
U	1.6	8.3	3.43	2.63

Note: <sup>a</sup>El Taher et al., 2007; <sup>b</sup>Renteria-Villalobos et al., 2010; <sup>c</sup>Da Conceição and Bonotto, 2006;

<sup>d</sup>Present study

The concentration of REE is very significant and as shown in Table 5, ranges from 0.16 ppm to 129.00 ppm or a mean value of 7.1 ppm. The concentration of the mean values of individual rare earth is: (La 24.51 ppm; Ce 33.54 ppm; Pr 4.72

ppm; Nd 19.35 ppm; Sm 3.72 ppm; Eu 0.95 ppm; Gd 3.78 ppm; Tb 0.59 ppm; Dy 3.54 ppm; Ho 0.74 ppm; Er 2.11 ppm; Tm 0.26 ppm; Yb 1.45 ppm; Lu 0.19 ppm).

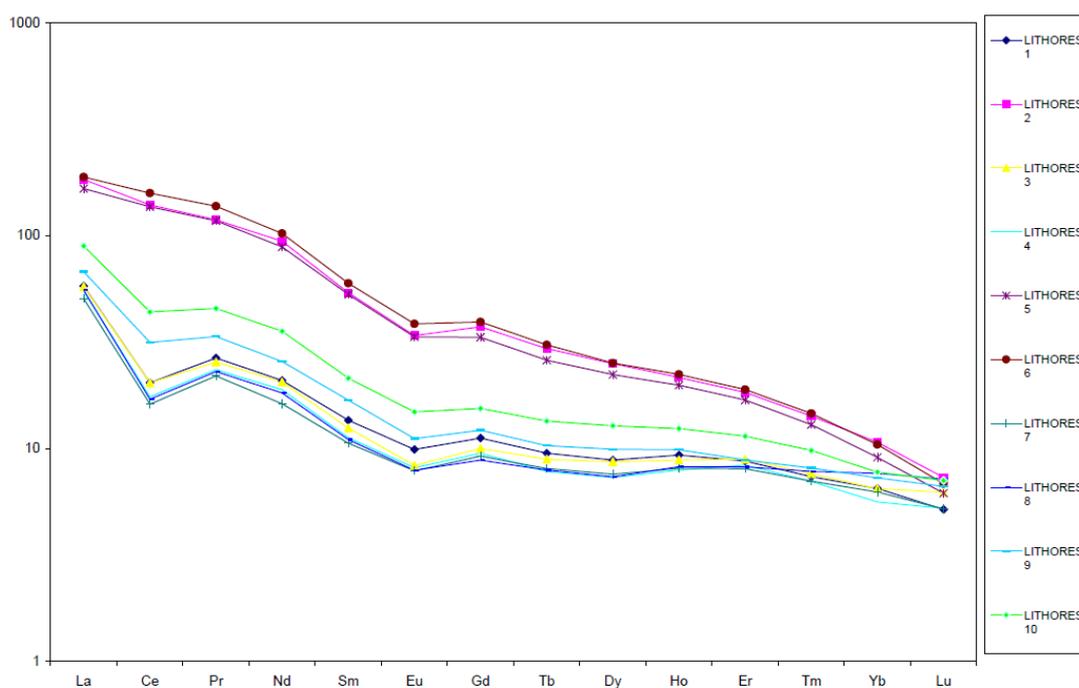
**Table 5**  
*Concentration of REE (ppm) in phosphorus gypsum from the HIV Veles dupm (FUS-ICP-MS)*

Elements	Average	Median	Min	Max	SD
La	24.51	18.70	11.90	59.30	13.51
Ce	33.54	17.10	10.80	129.00	35.17
Pr	4.72	2.98	2.01	15.40	3.86
Nd	19.35	12.50	8.73	61.00	15.60
Sm	3.72	2.57	1.75	11.40	2.91
Eu	0.95	0.66	0.40	2.78	0.67
Gd	3.78	2.90	2.08	10.20	2.39
Tb	0.59	0.47	0.32	1.50	0.34
Dy	3.54	2.87	1.98	8.19	1.84
Ho	0.74	0.63	0.44	1.56	0.32
Er	2.11	1.86	1.28	4.03	0.74
Tm	0.26	0.24	0.17	0.47	0.08
Yb	1.45	1.35	1.05	2.23	0.30
Lu	0.19	0.19	0.16	0.24	0.02

The established concentrations of elements from the REE group show significant quantities that can have an economic importance.

Therefore, in further research, it is necessary to investigate this phosphogypsum dump in detail using deep drilling methods and collecting a larger number of samples for a more detailed determi-

nation of the contents of the elements from the REE group. The distribution of the REE (Figures 3 and 4) shows many similarities with the distribution of rare elements in phosphorus rocks of sedimentary character, with expressed negative anomalies of Eu (Trape, J., 1967).



**Fig. 3.** Plot diagram of REE in phosphorus gypsum

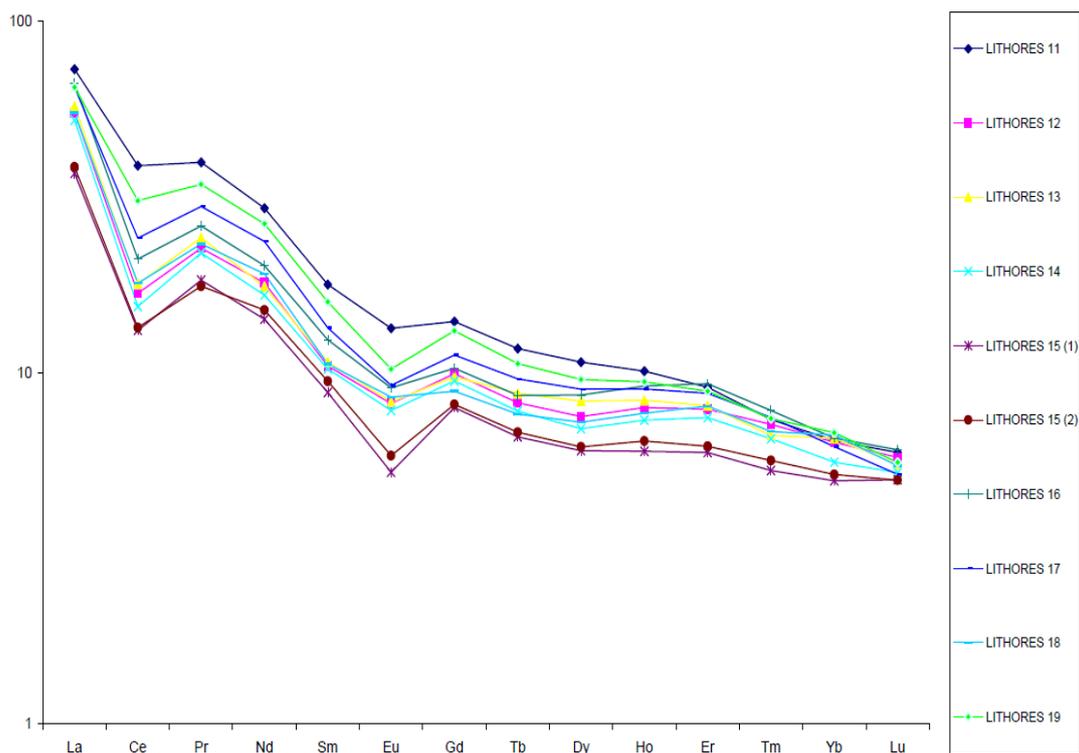


Fig. 4. Plot diagram of REE in phosphorus gypsum

### Mineralogical characterization

The testing of the mineralogical composition of the phosphogypsum using the XRD method (Table 6) shows that the main mineral phases are: gypsum, bassanite, anhydrite and quartz, with the percentage of gypsum being the largest ranging from 74.5% to 96.9%.

It is interesting to mention the percentage representation of quartz, ranging from 2.4% to 9.5%. The mineralogical composition tests performed using the SEM-EDS technique show the presence of the following mineral phases (Table 7): Calcium sulphate, Barium sulphate, Strontium sulphate, quartz, mica, zircon, fluorite, Fe, Ti-oxide and Fe-hydroxide.

Table 6

### Mineral abundances (wt %) in phosphorus gypsum from the HIV Veles dump

No.	Gypsum	Bassanite	Anhydrite	Quartz	No.	Gypsum	Bassanite	Anhydrite	Quartz
XRD 1	87.7	3.8	n.d.	8.5	XRD 11	90.5	n.d.	n.d.	9.5
XRD 2	97.6	n.d.	n.d.	2.4	XRD 12	93.0	n.d.	n.d.	7.0
XRD 3	74.5	16.6	3.0	6.0	XRD 13	94.2	n.d.	n.d.	5.8
XRD 4	92.6	n.d.	n.d.	7.4	XRD 14	92.0	n.d.	n.d.	8.0
XRD 5	91.2	3.3	n.d.	5.5	XRD 15	90.5	n.d.	n.d.	9.5
XRD 6	96.9	n.d.	n.d.	3.1	XRD 16	91.6	n.d.	n.d.	8.4
XRD 7	93.7	n.d.	n.d.	6.3	XRD 17	95.9	n.d.	n.d.	4.1
XRD 8	95.9	n.d.	n.d.	4.1	XRD 18	94.8	n.d.	n.d.	5.2
XRD 9	93.3	n.d.	n.d.	6.7	XRD 19	95.1	n.d.	n.d.	4.9
XRD 10	90.5	n.d.	n.d.	9.5	XRD 20	93.6	n.d.	n.d.	6.4

Note: n.d. = not detected

Table 7

SEM-EDS investigations of the phosphorus gypsum from the HIV Veles dump

	Mineral/Phase	SEM-EDS 1	SEM-EDS 2	SEM-EDS 3	SEM-EDS 4	SEM-EDS 5
Sulphate	Ca-sulphate	Major	Major	Major	Major	Major
	Ba-sulphate	Trace	Trace	Trace	Trace	Trace
	Sr-sulphate	n.d.	n.d.	n.d.	n.d.	Trace
Silicate	Quartz	Minor	Major	Major	Major	Major
	Mica	n.d.	Trace	n.d.	n.d.	n.d.
	Zircon	n.d.	n.d.	n.d.	Trace	n.d.
Other	CaF <sub>2</sub> – Fluorite	Trace	Minor	Minor	Minor	Trace
	Fe, Ti-oxide	n.d.	Trace	n.d.	n.d.	n.d.
	Fe-hydroxide	Trace	n.d.	n.d.	n.d.	n.d.

The morphological forms of the present mineral phases are shown in Figure 5. The chemical compositions of the mineral phases of Ca-sulphate (Figure 6), Ba-sulphate (Figure 7), Sr-sulphate (Figure 8) and fluorite (Figure 9) are determined

using the SEM-ED technique. The three sulphate phases could, tentatively, be considered as altered gypsum (anhydrite), altered barite and altered celestine. The "CaF<sub>2</sub>" entry includes both the amorphous and crystalline.

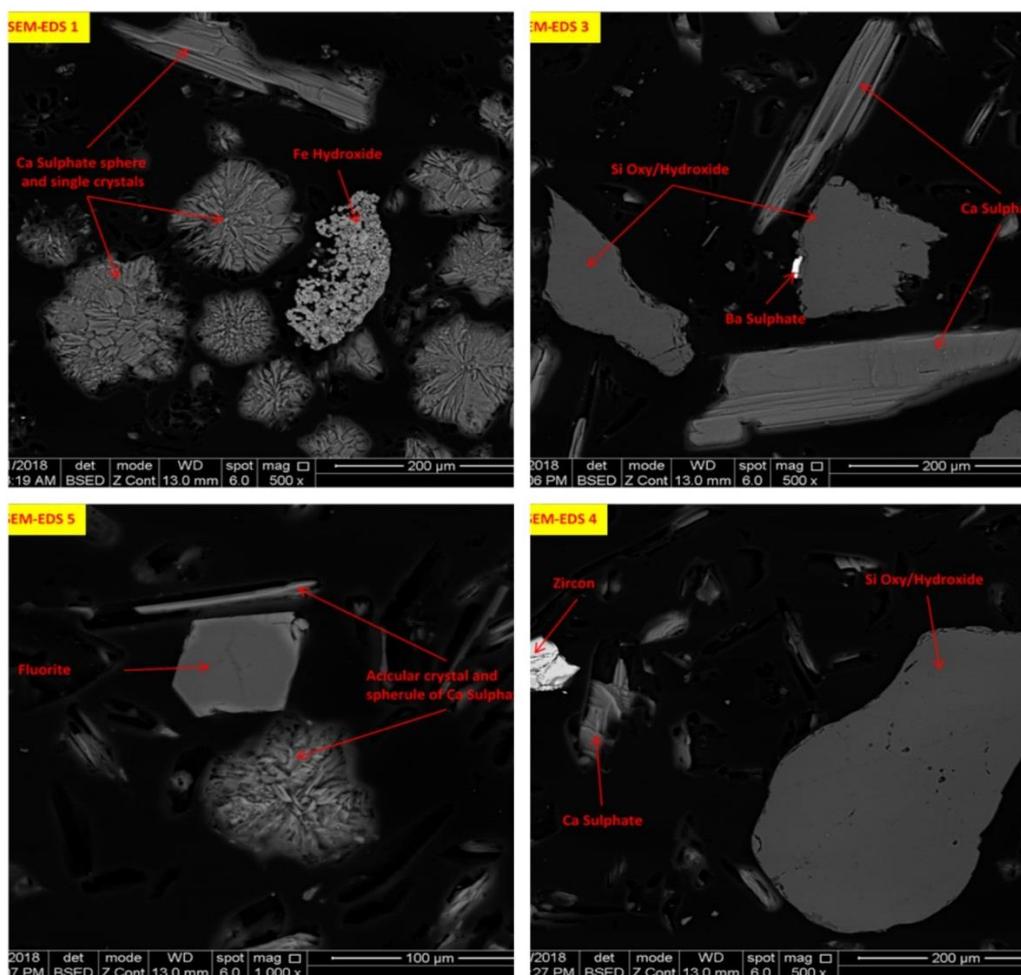


Fig. 5. SEM-EDS observations of phosphorus gypsum

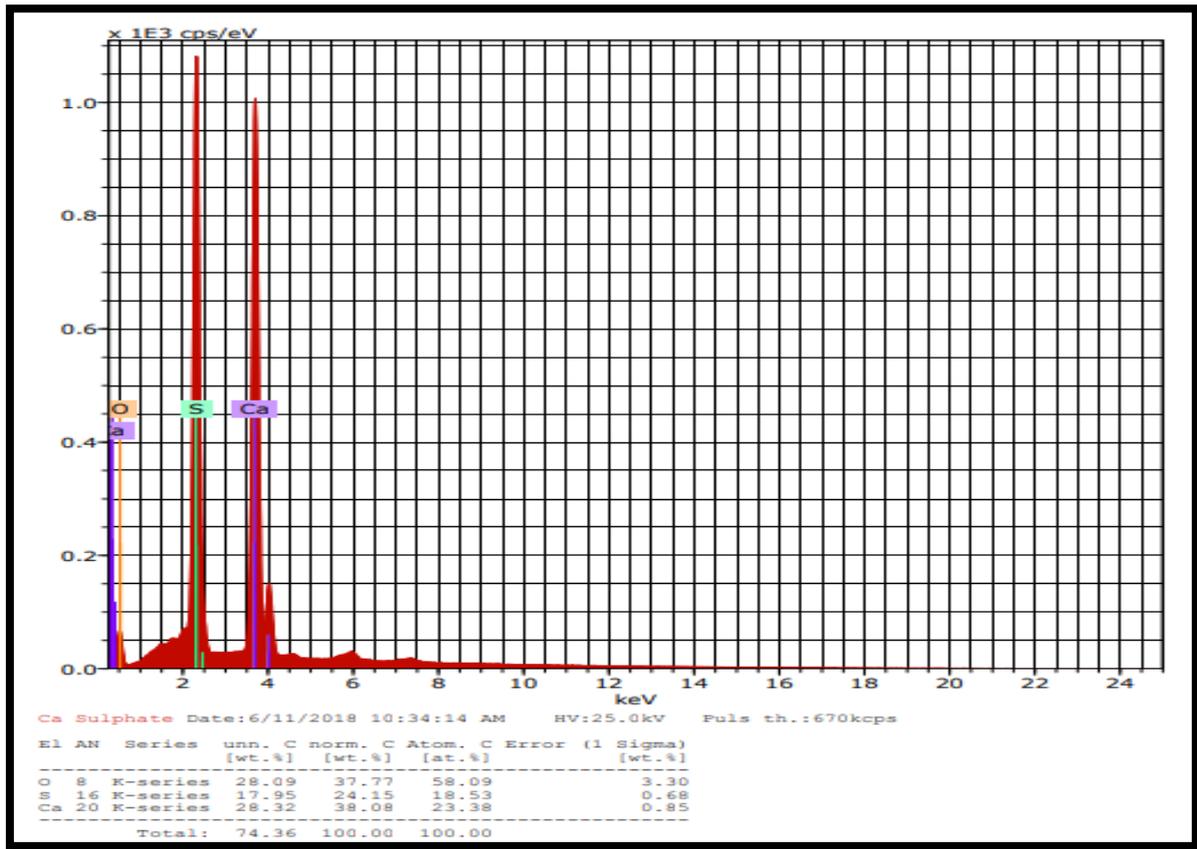


Fig. 6. SEM-EDS composition of Ca-sulphate

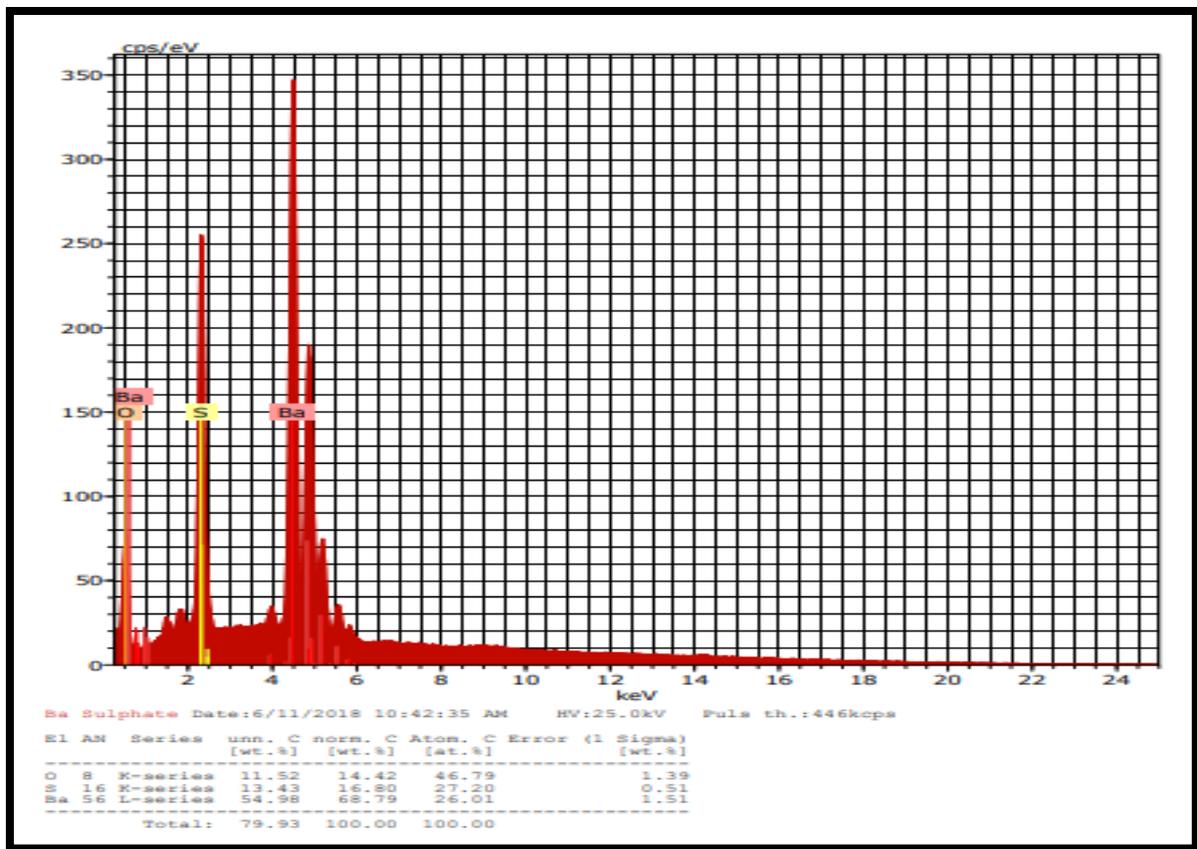


Fig. 7. SEM-EDS chemical composition of Ba-sulphate

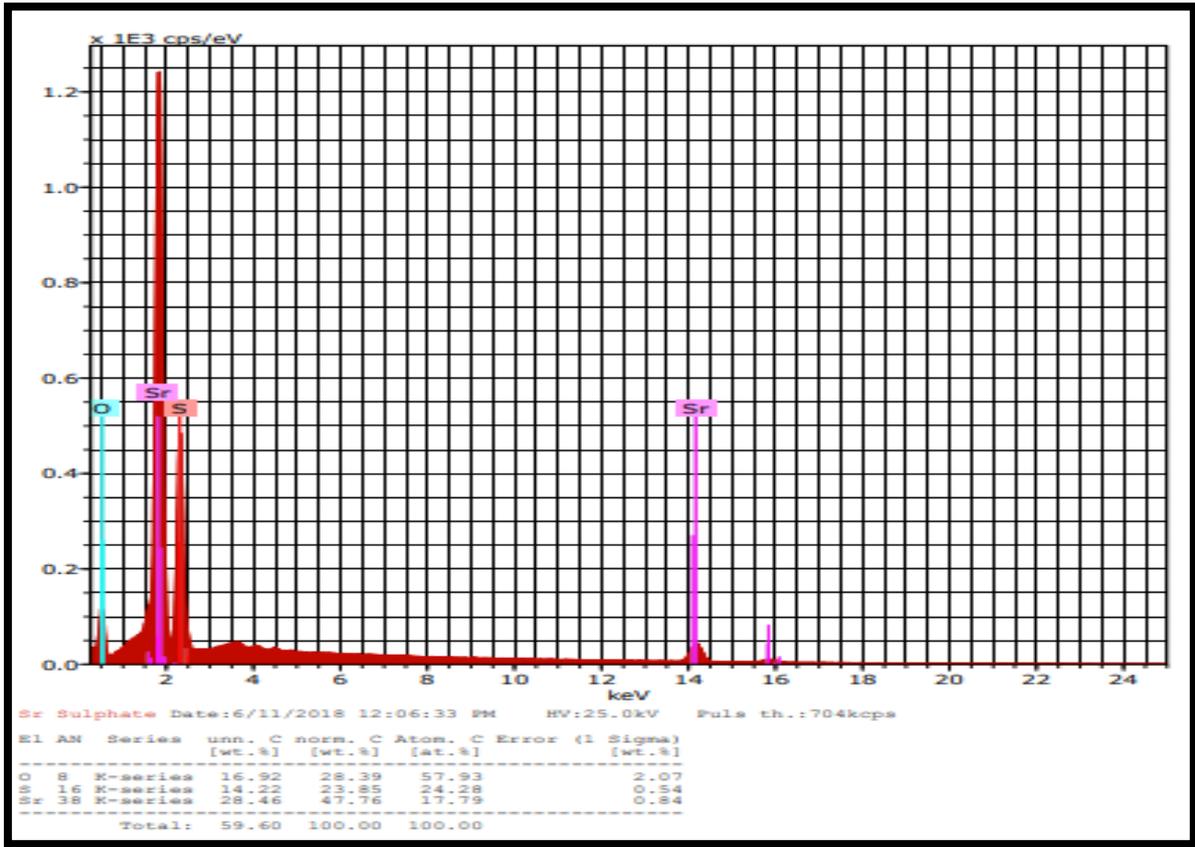


Fig. 8. SEM-EDS chemical composition of Sr-sulphate

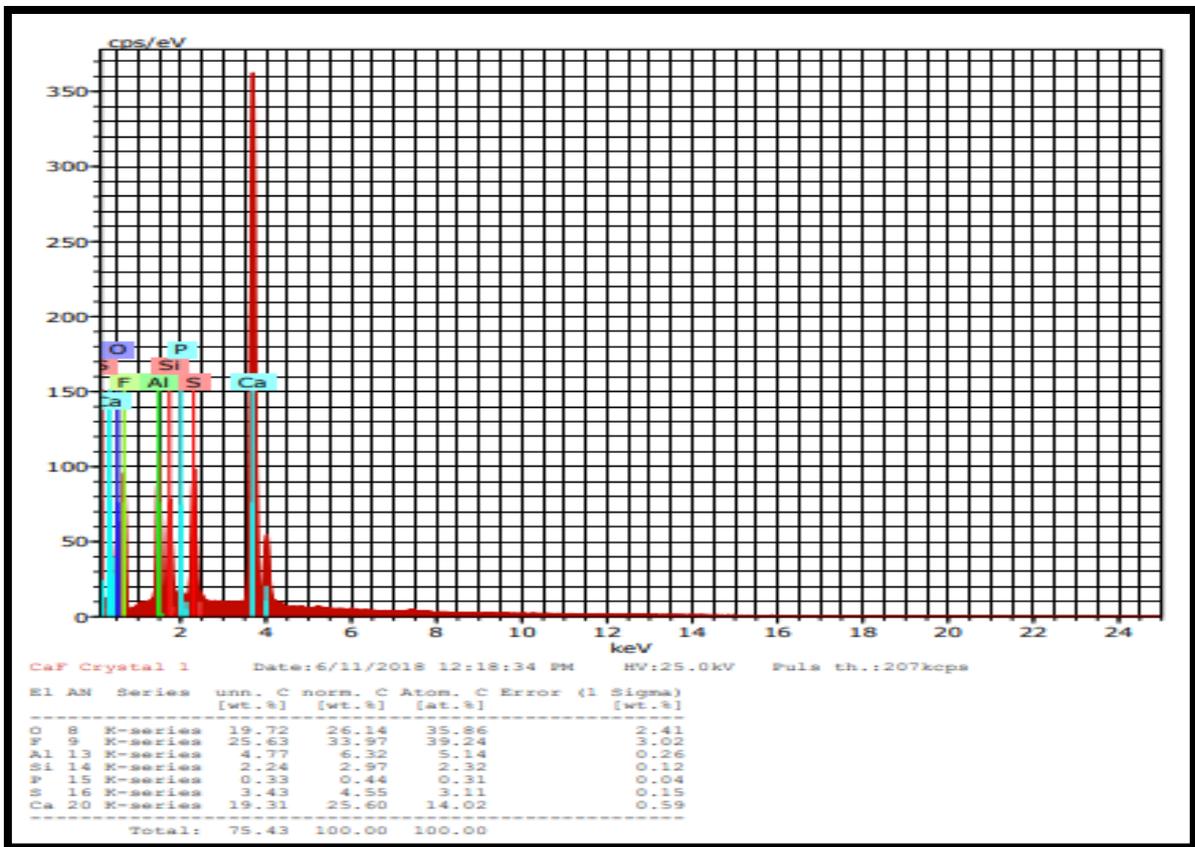


Fig. 9. SEM-EDS composition of CaF<sub>2</sub> crystals

**Radiological investigations**

Table 8 shows the results of the measured activities in the five samples together with the basic descriptive statistics.

Table 8

*Results of the measurements and the basic descriptive statistics of the five phosphogypsum samples (Bq/kg)*

	Total α	Total β	<sup>40</sup> K	<sup>232</sup> Th	<sup>238</sup> U	<sup>226</sup> Ra
1	1090	1610			300	200
2	980	1740			400	300
3	980	1980			400	400
4	820	1380			300	200
5	880	1760			400	300
Arithmetic mean	950	1694	<1000	<10	360	280
Minimum	820	1380			300	200
Maximum	1090	1980			400	400
Standard deviation	104	220			55	84
Variation coefficient	11%	13%			15%	30%

The results indicate that the total alpha and beta activities were measured in all samples and that they mainly derived from isotopes from the array <sup>238</sup>U. The specific activities of the <sup>40</sup>K and <sup>232</sup>Th array isotopes were below detection level. The variations between the total alpha and beta activities, as well as <sup>238</sup>U activities in the five samples are in the range of 11% to 15% and are lower in relation to the variations of <sup>226</sup>Ra at 30%.

Values of measured specific activities higher than natural ones were provable by comparing them with the results published in previous studies conducted in the Republic of N. Macedonia. The mean values of the measured total alpha and beta specific activities in the phosphogypsum were higher in relation to the corresponding mean activities published for soils sampled in the vicinity of Veles (Dimovska et al., 2010) (Figure 10). The activities of <sup>238</sup>U were higher than the values obtained for soils in Veles (Dimovska et al., 2010) and higher than the average values for the whole of N. Macedonia (Stojanovska, 2010) (Figure 10).

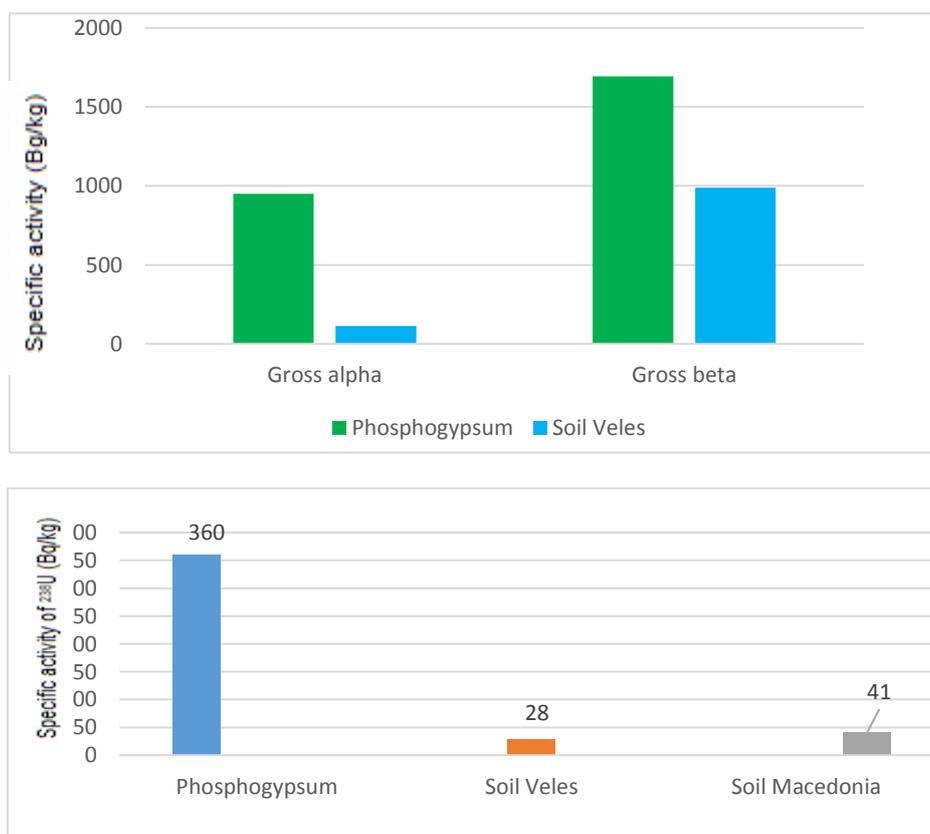


Fig. 10. Comparison of the results of specific activities in phosphogypsum and soils from the Republic of North Macedonia

A number of studies are found in the literature, in which the content of radionuclides in the phosphogypsum and its application have been studied. Mainly, as in this study, the specific activities of  $^{232}\text{Th}$  and  $^{40}\text{K}$  are lower than the radionuclide values from the  $^{238}\text{U}$  array. On the other hand, the published activities of  $^{226}\text{Ra}$  are generally higher than  $^{238}\text{U}$ , which is not the case in our study. Figure 10 shows the values of the specific activities of  $^{226}\text{Ra}$  in the phosphogypsum of some earths compared to the average value of  $^{226}\text{Ra}$  in this study. The values of  $^{226}\text{Ra}$  in phosphogypsum from Egypt (Khalifa and

El-Arabi, 2005), Croatia (Bituh et al., 2009), Jordan (Zieliński et al., 2011), Slovenia (Kobal et al., 1990), Spain (Lopez-Coto et al., 2014), Greece (Papageorgiou et al., 2016) and Serbia (Rajković and Tošković, 2002) are higher compared to the results of this study.

In accordance with the data from the literature (e.g. Campos et al., 2017; Mesić et al., 2016; Rashad, 2017; Saadaoui et al., 2017), further use of phosphogypsum in construction and agriculture is not excluded.

## CONCLUSION

The detailed investigations of the chemical, geochemical, mineralogical and radiological composition of the phosphogypsum from the HIV Veles dump show that it is a chemically, geochemically, mineralogically and radiologically uniform material. The mineral composition is simple and dominated by gypsum and there is very little presence of accessory minerals (quartz, Ba-sulphate, Sr-sulphate, fluorite, zircon, mica).

The high representation of REE, often reaching 300 ppm, points to the fact that this material is a serious raw material with a high proportion of elements from the REE group and that it is an economically interesting raw material.

Based on radiological testing, the following conclusions can be made:

- The total alpha and beta specific activities in the dump are higher compared to their values in soils from Veles and the surrounding area.

- The specific activities of  $^{40}\text{K}$ , as well as of the radioisotopes of the  $^{232}\text{Th}$  array were below the detection level. The presence of  $^{238}\text{U}$  and  $^{226}\text{Ra}$  with activities higher than the activities in soils has been identified.

- The arithmetic mean value of the specific activity of  $^{226}\text{Ra}$  in this study is lower in relation to the values published in studies conducted in other countries.

## REFERENCES

- Al-Hwaiti, M. S., Brumsack, H. J., Schnetger, B. (2015): Fraction distribution and risk assessment of heavy metals in waste clay sediment discharged through the phosphate beneficiation process in Jordan. *Environ Monit Assess*, **187** (7), 401, DOI: 10.1007/s10661-015-4579-2
- Al-Masri, M. S., Amin, Y., Ibrahim, S., Al-Bich, F. (2004): Distribution of some trace metals in Syrian phosphogypsum. *Appl Geochem.*, **19**, 747–753.
- Bituh, T., Marović, G., Franić, Z., Sencar, J., Bronzović, M. (2009): Radioactive contamination in Croatia by phosphate fertilizer production. *J. Hazard. Mater.*, **162** (2–3), 1199–1203.
- Campos, M. P., Costa, L. J. P., Nisti, M. B., Mazzilli, B. P. (2017): Phosphogypsum recycling in the building materials industry: assessment of the radon exhalation rate. *Journal of Environmental Radioactivity*, **172**, 232–236.
- Da Conceição, F. T., Bonotto, D. M. (2006): Radionuclides, heavy metals and fluorine incidence at Tapira phosphate rocks, Brazil, and their industrial (by)products. *Environ. Pollut.*, **139** (2), pp. 232–243.
- Değirmenci, N., Okucu, A. (2007): Usability of fly ash and phosphogypsum in manufacturing of building products. *Journal of Engineering Sciences*, **13** (2), 273–278.
- Dimitrioski, T. (2011): *Installation for production of artificial fertilizers HIV Zgropolci, Gradsko municipality*. Metrumhem DOOEL Skopje, 25 p.
- Dimovska, S., Stafilov, T., Šajn, R., Frontasyeva, M. (2010): Distribution of some natural and man-made radionuclides in soil from the city of Veles (Republic of Macedonia) and its environs. *Radiation Protection Dosimetry*. Vol. **138**. N6. 2, pp. 144–157, DOI: 10.1093/rpd/ncp238.
- El-Taher, A., Uosif, M. A., Orabi, A. A. (2007): Natural radioactivity levels and radiation hazard indices in granite from Aswan to Wadi El-Allaqi southeastern desert, Egypt. *Radiat Prot Dosimetry*, **124** (2), 148–54 DOI: 10.1093/rpd/ncm211
- El Zrelli, R., Rabaoui, L., Daghbouj, N., Abda, H., Castet, S., Josse, C., Van Beek, P., Souhaut, M., Michel, S., Bejaoui, N., Courjault-Radé, P. (2018): Characterization of phosphate rock and phosphogypsum from Gabes phosphate fertilizer factories (SE Tunisia): high mining potential an implication for environmental protection. *Environ. Sci. Pollut. Res. Int.*, **25** (15), 14690–14702. DOI: 10.1007/s11356-018-1648-4.
- Kacimi, L., Simon-Masseron, A., Ghomari, A., Derriche, Z. (2006): Reduction of clinkerization temperature by using phosphogypsum. *Journal of Hazardous Materials*, **137** (1), 129–137.
- Khalifa, N. A., El-Arabi, A. M. (2005): Natural radioactivity in farm soil and phosphate fertilizer and its environmental implications in Qenagovernate, Upper Egypt. *Journal of Environmental Radioactivity*, **84** (1), 51–64.

- Kobal, I., Brajnik, D., Kaluža, F., Vengust, M., (1990): Radionuclides in effluent from coal mines, a coal-fired power plant, and a phosphate processing plant in Zasavje, Slovenia (Yugoslavia). *Health Physics*, **58** (1), pp. 80–85.
- Lopez-Coto, I., Mas, J. L., Vargas, A., Bolívar, J. P. (2014): Studying radon exhalation rates variability from phosphogypsum piles in the SW of Spain. *Journal of Hazardous Materials*, **280**, 464–471.
- Mesić, M., Brezinscak, L., Zgorelec, Z., Perčin, A., Šestak, I., Bilandzija, D., Trdenić, M., Lisac, H. (2016): The application of phosphogypsum in agriculture. *Agriculturae Conspectus Scientificus*, **81** (1). 7–13.
- Papageorgiou, F., Godelitsas, A., Mertzimekis, T. J., Xanthos, S., Voulgaris, N., Katsantonis, G. (2016): Environmental impact of phosphogypsum stockpile in remediated schistos waste site (Piraeus, Greece) using a combination of  $\gamma$ -ray spectrometry with geographic information systems. *Environ. Monit. Assess.*, **188** (3), 133.
- Rajković, M. B., Tošković, D. V. (2002): Investigation of the possibilities of phosphogypsum application for building partitioning walls-elements of a prefabricated house. *Acta Periodica Technologica*, **33**, 71–92.
- Rashad, A. M. (2017): Phosphogypsum as a construction material. *Journal of Cleaner Production*, **166**, 732–743.
- Reguigui, R., Sfar Felfoul, H., Ben Ouedzou, M., Clastres, P. (2005): Radionuclide levels and temporal variation in phosphogypsum. *J. Radioanal. Nucl. Chem.*, **264** (3) 719–722.
- Rentería-Villalobos, M., Vioque, I., Mantero, J., Manjón, G. (2010): Radiological, chemical and morphological characterizations of phosphate rock and phosphogypsum from phosphoric acid factories in SW Spain, *Journal of Hazardous Materials*, **181** (1–3), 193–203, DOI: 10.1016/j.jhazmat.2010.04.116. Epub 2010 May 7
- Saadaoui, E., Ghazel, N., Romdhane, C., Massoudi, N. (2017): Phosphogypsum: potential uses and problems – A review. *International Journal of Environmental Studies*, **06**, 19.
- Stojanovska, Z., Nedelkovski, D., Ristova, M. (2010): Natural radioactivity and human exposure by raw materials and end product from cement industry used as building materials, *Radiation Measurements*, Vol. **45**, No. 8, pp 069–972.
- Trape, J. (1967): *Phanerozoic Phosphorite Depositional Systems*, Springer, pp 9–58.
- Zieliński, R. A., Al-Hwaiti, M. S. (2011): Radionuclides, trace elements, and radium residence in phosphogypsum of Jordan. *Environmental Geochemistry and Health*, **33**, 149–165.

## Резиме

## КАРАКТЕРИЗАЦИЈА НА ФОСФОРНИОТ ГИПС ОД ДЕПОНИЈАТА НА ФАБРИКАТА ЗА ПРОИЗВОДСТВО НА ВЕШТАЧКИ ЃУБРИВА ВО ВЕЛЕС (СЕВЕРНА МАКЕДОНИЈА) И ВЛИЈАНИЕ ВРЗ ЖИВОТНАТА СРЕДИНА

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**Клучни зборови:** фосфорен гипс; вештачки ѓубрива; минералшки; алфа и бета специфична активност

Работата на фабриката за производство на вештачки ѓубрива во околината на Велес (Република Северна Македонија) резултираше со остаток од околу 3.4 милиони тони фосфорен гипс депониран на депонијата во непосредна близина на фабриката во периодот од 1980 до 2003 година. Досега не е извршена ремедијација на депонијата на фосфорен гипс. Во овој труд се прикажани резултатите добиени од репрезентативни примероци земени од депонијата со примена на методите: аналитички методи (ICP-MS, FUS-ICP-MS), минералшки методи, рендгенска дифракција

(powder-XRD), електронска микроскопија (SEM-EDS), како и спектрометрија со  $\gamma$ -зраци со висока резолуција. Примероците содржат кристален гипс (Са-сулфат), Fe-хидроксид, Ва-сулфат, Са-флуорит, Si-оксихидроксид и циркон. Вкупната алфа специфична активност се движи од 820 Bq/kg до 1090 Bq/kg, со просечна вредност од  $950 \pm 104$  Bq/kg, а специфичната бета активност е во интервалот од 1380 Bq/kg до 1980 Bq/kg, со просечна вредност од  $1694 \pm 220$  Bq/kg.