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GEOLOGICAL AND TECHNOLOGICAL CHARACTERISTICS OF THE IGROŠ-VIDOJEVIĆI ZEOLITE TUFF DEPOSITS

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Abstract

In this work presents investigations of zeolitic tuff samples from the "Igroš-Vidojevići" deposit. The aim of the research was to determine the quality of samples taken from all deposit parts. Thus, samples were taken from the footwall ("Zeolit 1"), and four samples from the central deposit part ("Zeolit 2", "Zeolit 3", "Zeolit 4" and "Zeolit 5"). Characterization of the samples included chemical analysis, determination cation-exchange capacity (CEC), X-ray powder diffraction analysis (XRPD) and differ- ential thermal and thermogravimetric analysis (DTA and TGA). Results have shown that the footwall consists mostly of clays, whereas zeolite minerals dominate in the rest of the deposit.

***Key words**: Zeolite, Igroš-Vidojevići deposit, cation- exchange capacity, thermal analysis, X-Ray powder diffraction analysis*

1. INTRODUCTION

A large number of occurrences and deposits of natural zeolites of pyroclastic origin, widely distributed in Miocene sediments of Serbia, such as Zlatokop (Vranj basin), Igroš, Jablanica 1 (Kruševački basin), Beočin (Fruška Gora), Toponica (Kosovska Kamenica), and Slanci (Danube key near Belgrade), are spatially and genetically related to volcanic and volcaniclastic rocks of marine environments of Senonian and Neogene age and lake sediments of Neogene age [1,5]. The zeolitic tuff deposits were created as a product of the devitrification of volcanic glass. The lake environment had a great influence on the diagenesis of the sediments and the formation of clinoptilolites at the expense of volcanic glass. The zeolitic tuffs themselves are mostly composed of zeolitic minerals of the HEU-type clinoptilolite-hoylandite series, which are present in the form of small acicular to plate-like crystals with dimensions from 0.1 to 100 μm.

2. GEOLOGY OF THE ZEOLITIC TUFF DEPOSIT IN IGROS

The Igroš zeolitic tuff deposit covers the southernmost edge of the Miocene Kruševac basin. In the deposit area, two ore fields [2] have been identified: Šovići-Đorđevići and Igroš-Vidojevići.

Igroš-Vidojevići ore field: The zeolitic layer of tuff stretches from the northwest to the southeast and can be followed intermittently for a length of 1.1 km. Geological investigations [2] at the "Igroš-Vidojevići" ore field identified two ore bodies: "ore body 1" and "ore body 2".

The mapping of the terrain, as well as the exploitation works on "ore body 1" revealed that the layer of zeolitized tuff extends in a north-south direction and can be followed for about 170 m along its length and about 50 m on average. The layer of zeolitized tuff is interstratified within the

Miocene-Pliocene series of marly green clays that comprise the basement, as well as the brown clays and green sandstones that form the bedrock. The zeolitic tuff layer is light gray to white with an average thickness of 1.64 m, with a general north-south strike and a mean statistical dip to the north at an angle of about 4 °. The samples of zeolitic tuff that were used for the tests presented in the paper were taken from the exploitation field "Igroš-Vidojevići" - atar of the village of Igroš. 5 samples were selected for analysis: the sample marked "Zeolite 1" is a representative sample of the bottom of the deposit, while the samples marked "Zeolite 2, 3, 4, and 5" belong to the central part of the deposit. "Zeolite 2" and "Zeolite 5" are representative samples created by crushing excavated tuff, sample "Zeolite 3" is formed from crushed tuff of class 100+30 mm, and "Zeolite 4" is a sample of size -100 μm obtained by grinding.

3. RESULTS AND DISCUSSION

X-ray analysis

The mineral composition of the samples was determined by the X-ray powder diffraction (XRD) method using a "Philips" powder diffractometer, model PW-1710. Since all samples of zeolite tuffs (Zeolite 2, 3, 4, and 5) have a very similar mineralogical composition, two characteristic X-ray diffractograms of zeolite samples 2 and 4 are shown in Figure 1. Namely, the presence of zeolite minerals of the clinoptilolitic type, quartz, feldspar, and mica was determined in all analyzed samples. Feldspars and quartz are far less present, while micas are present in traces.

Chemical composition

The results of the chemical analysis of the examined samples using the AAS method (classical chemical analysis for aluminosilicates [3]) are shown in Table 1 [4]. The results show that in addition to the structural elements (silicon and aluminum), the tested samples also contain Ca, Mg, Na, and K. Also, a significant presence of iron is noted, especially in the sample "Zeolite 1", which is expected considering the volcanic origin of this rock mass. The content of other heavy metals in all examined samples (Pb, Mn, Cu, Zn, Cd, Sb, Cr, and Sn) is relatively low.

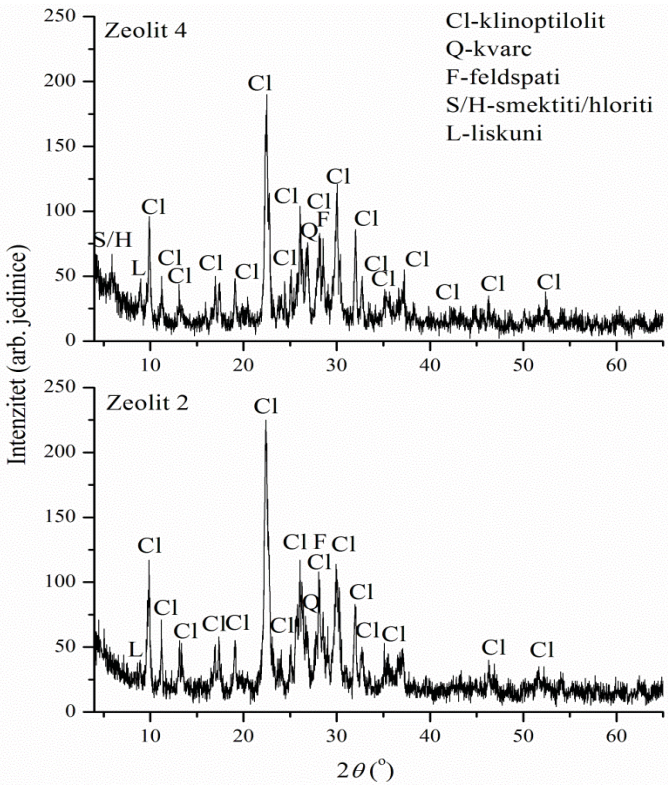

Figure 1. X-ray diffractograms of "Zeolite 2 and 4" samples of zeolite tuff from the "Igroš-Vidojevići".

Table 1. Chemical composition of samples from the "Igroš-Vidojevići" zeolite tuff deposits

Component, mas. %	Zeolite 1	Zeolite 2	Zeolite 3	Zeolite 4	Zeolite 5
SiO_2	49,76	63,52	62,88	65,58	60,41
Al_2O_3	21,04	15,32	15,26	10,68	16,46
CaO	2,27	4,71	4,90	4,90	4,19
MgO	4,78	1,55	1,90	2,06	1,91
Fe_2O_3	7,58	1,00	1,82	3,00	2,44
K_2O	4,20	0,93	0,87	1,21	1,41
Na_2O	2,15	1,13	1,13	1,23	1,56
TiO_2	1,17	0,337	0,337	0,839	1,52
PbO	0,0059	0,0038	0,0051	0,0037	0,0096
MnO	0,046	0,017	0,022	0,042	0,034
Cu	0,008	0,011	0,066	0,033	0,064
Zn	0,016	0,0053	0,011	0,0054	0,012
Cd	0,0002	0,0003	0,0002	0,0001	0,00014
Sb	0,005	0,004	0,004	0,0037	0,007
Cr	0,009	0,0003	0,0005	0,0012	0,0013
Sn	<0,0005	<0,0005	<0,0005	<0,0005	<0,0005
Loss on Ignition (T_{max}=900 ^{0C})	6,95	11,42	10,79	10,41	9,97

Cation exchange capacity (CEC)

Cation exchange capacity (KKI-CEC) was determined by the standard method with 1 mol/dm3 NH4Cl [6]. In the case of zeolite, the ions that participate in the exchange are Ca2+, Mg2+, Na+ and K+, while their sum determines the total capacity, which is expressed in mmol/100 g. The total KKI is 141.99 mmol/100 g, followed by the sample "Zeolite 3" which is 121.01 mmol/100 g. The CEC of the "Zeolite 4" sample is slightly lower, 89.48 mmol/100 g, and is close to the CEC of the "Zeolite 5" sample (83.75 mmol/100 g). The smallest CEC was obtained for the bottom sample - "Zeolite 1" and is 46.98 mmol/100 g, which indicates that clay mass dominates in this part of the deposit (Table 2).

Table 2. Results of the cation exchange coefficient (CEC / mmol (100 g)–1) of zeolitic tuff samples

Zeolite	Na	K	Ca	Mg	Σcation
1	6,18	1,75	31,56	7,49	46,98
2	29,71	12,66	90,57	9,05	141,99
3	19,05	8,18	87,82	5,96	121,01
4	11,31	6,34	65,87	5,96	89,48
5	23,38	9,85	43,36	7,16	83,75

Thermal analysis (TG and DTA)

Thermal analysis provides information on the dehydration processes, dehydroxylation, and thermal stability of aluminosilicate minerals. Figure 4 shows the comparative characteristic TG/DTG/DTA diagrams of zeolitic tuff samples 1, 2, and 3. Continuous mass loss is observed in the temperature range from 25 to 1000 ºC. The loss of mass on the TG diagram in the temperature range up to 300 ºC comes from the release of water bound to various cation centers in the zeolite channels or on the surface (dehydration). On the DTA diagrams of the "Zeolite 2 and 3" samples, in the temperature interval from 25 to 300 ºC, one endothermic peak with a minimum at ≈130 ºC, originating from dehydration, and a bend at ≈220 ºC, which are characteristic of calcium zeolite [7], can be observed. "Zeolite 1" is significantly different from the diagrams of the other examined

samples. This type of TG and DTA diagram indicates the presence of clay minerals in the sample "Zeolite 1".

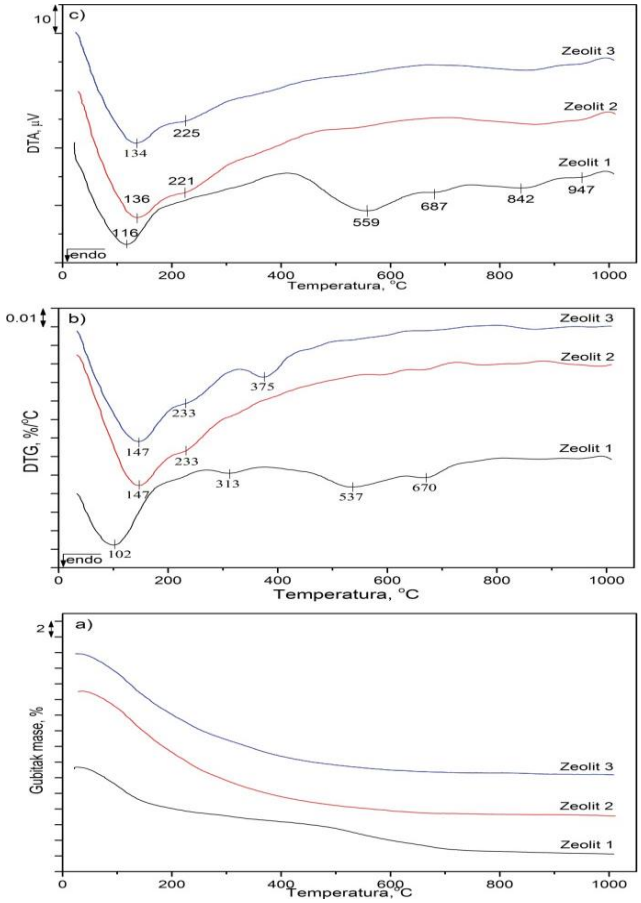

Figure 2. Thermal analysis of „Zeolite 1“, „Zeolite 2“ and„Zeolite 3“. a) TGA; b) DTG; c) DTA.

Results of infrared spectroscopy analysis

FTIR analysis confirmed the presence of hydrated aluminosilicates in the tested samples. The results showed the absence of any significant differences in the infrared spectra of the tested samples. For this reason, only one representative spectrum is shown and explained in Figure 3. In the infrared spectrum, the bands in the frequency range from 1150 to 400 cm^{-1} are the result of structural vibrations. Thus, the band at 1005 cm^{-1} originates from the asymmetric stretching vibrations of the Al–O–Si group, which in clinoptilolite-type zeolites usually occur at frequencies from 1150 to 930 cm^{-1}.

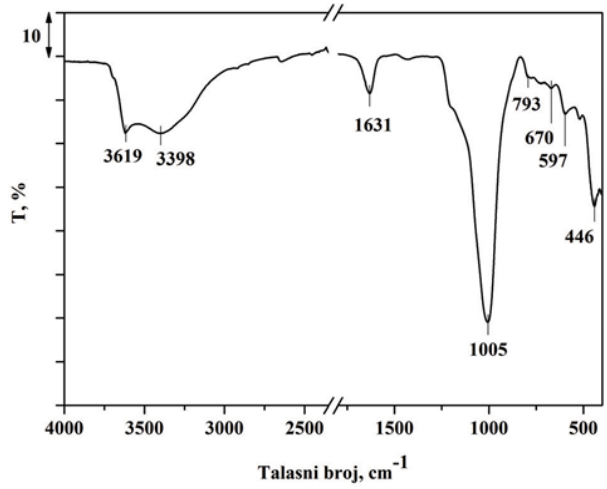

Figure 3. FTIR diagram of the sample from the “Igroš-Vidojevići” zeolite tuff deposit.

4. CONCLUSION

The largest part of the floor of the zeolite tuff deposit "Igroš-Vidojevići" is made up of clay, while in other parts, zeolite dominates. The X-ray analysis of the "Zeolite 1" sample revealed the presence of the clay minerals smectite and kaolinite. In the samples that belong to the central part of the "Zeolite 2-5" deposit, XRD and SEM/EDS analyses revealed the presence of zeolite-clinoptilolite, and the clay mineral content is less than 10%. The results of the infrared spectroscopic analysis indicated a slightly lower presence of quartz in the samples "Zeolite 2-5" compared to the sample "Zeolite 1". The results of thermal analysis (DTA and TG diagrams) of the "Zeolite 1" sample indicate the presence of clay minerals at the bottom of the deposit. For "Zeolite 2–5" samples, peaks characteristic of clinoptilolite appear in the DTA diagram.The results of determining the cation exchange capacity showed that the CEC of the sample "Zeolite 1" was the lowest, and was 46.98 mmol/100 g, which confirms the conclusion that the clay mass is located at the bottom. The highest CEC was obtained for the samples "Zeolite 2" and "Zeolite 3", 141.99 and 121.01 mmol//100 g, respectively, which corresponds to clinoptilolite. The results of determining the chemical composition and heavy metal content showed that Fe2O3 in the sample "Zeolite 1" increased to 7.58%. Therefore, further research will be based on finding a way to remove the magnetic impurities to exploit this clay part of the deposit.

Based on the results obtained, it can be concluded that zeolite taken from any part of this deposit, except from the bottom, can be valorized and applied for certain purposes. Due to the high cation exchange capacity and content of zeolite minerals, samples with a CEC greater than 120 mmol/100 g ("Zeolite 2" and "Zeolite 3") may have potential application in wastewater treatment or decontamination of animal feed. Zeolite with a CEC of up to 90 mmol/100 g ("Zeolite 4" and "Zeolite 5") can be used for improving soil quality and the like.

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