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52nd International October Conference on Mining and Metallurgy

PROCEEDINGS

Edited by

Saša Stojadinović

and

Dejan Petrović

November 29th – 30th 2021

Bor, Serbia

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GEOLOGICAL AND MINERAL CHARACTERISTICS OF ZEOLITHIC TUFF TOPONICA DEPOSITS NEAR KOSOVSKA KAMENICA

Vladan Kašić[1], Ana Radosavljević-Mihajlović[1], Slobodan Radosavljević[1], Jovica Stojanović[1], Slavica Mihajlović[1], Melina Vukadinović[1]

[1]Institute for Technology of Nuclear and Other Raw Mineral Materials, Applied Mineralogy Unit, P.O. Box 390, Franschet d'Esperey 86, 11000 Belgrade, Serbia

Abstract

Zeolites are a group of natural and artificial inorganic compounds, which have specific physicochemical properties appropriate for industrial application. These minerals make a specific group of alumosilicates within tectosilicates because of their origin, chemical compositions, structural characteristics and application. This paper presents the results of mineralogical and crystallographic examination of zeolite tuff samples from the Toponica deposit. The deposit of zeolite tuff "Toponica" is located in the extreme eastern part of Kosmet near Kosovska Kamenica. The immediate geological structure of the zeolite tuff deposit consists of the Lower Miocene (M) clayey sandstone, the horizon of the white zeolite tuff and the reclassified Miocene clays, clays and gravel. The basic mineral composition is the mineral clinoptilolite-Ca from the heylandite series.

***Keywords**: Toponica, zeolitic tuff, clinoptilolite-heulandite group.*

1. INTRODUCTION

Studies have shown that zeolite deposits according to genetic characteristics belong to diagenetic deposits (volcanic-sedimentary) and hydrothermal-metasomatic deposits (with volcanic formations) [1-3]. In the deposits of marine and lake sediments, zeolites are mainly formed in the reaction of water with solid materials. The most present solid material (reactant) is volcanic glass, and the second reactant can be amorphous phase, poorly crystallized clays, montmorillonite, minerals of the plagioclase group, nepheline, quartz or silicon of biogenic origin. Clay minerals and zeolite minerals can be formed from the same material, and whether one or another mineral will crystallize will depend on the physico-chemical conditions of the given environment.

Thanks to the dimensions of their channels, zeolites absorb only those molecules whose sizes correspond to the dimensions of cavities, which is why they are called molecular sieves. Adsorption and molecular sieves are used in numerous processes of extracting harmful or useful components from gaseous phases, for the purpose of separation, purification and drying of gases.

Numerous technological processes are based on the properties of ion exchange, and have found application in the extraction of harmful components from wastewater or natural waters, in the processes of drinking water purification. The reactivity of the molecules increases, as a result of which zeolites exhibit intense catalytic activity. Based on that, they have found application in reactions in the processing of natural gas, petroleum raw materials, obtaining various products in the processes of organic synthesis [5].

2. METHODS

For mineralogical and crystallographic analyzes, flat samples were used and prepared under the same conditions up to grain size + 100% -63μm. A polarizing microscope ("JENAPOL-U" Zeiss-Jena), in transmitted light, by the immersion method, was used for mineralogical analysis.

A scanning electron microscope (SEM-PHILIPS ™ XL20) with an EDS component (Energy Dispersion X-ray, EDX) was used to observe the morphological properties and determine the chemical composition of the zeolite tuff. X-ray analysis was performed on an automatic diffractometer "PW-1710", using Cu tubes at a voltage of 40 kV and a current of 30 mA for powder.

3. RESULTS AND DISCUSSION

3.1 Geology of the Toponica deposit

The deposit of zeolite tuff "Toponica" is located in the extreme eastern part of Kosovo, near Kosovska Kamenica. Regionally, the examined area belongs to the tectonic unit of the Serbian-Macedonian metallogenetic province. This area is characterized by intense magmatic activity from the Paleozoic to the Tertiary, when the largest complexes of dacito-andesitic rocks of Novo Brdo and the surrounding area were cast.

The geological structure of the wider area of zeolite tuff deposits consists of: crystalline shales and migmatites, garnets, pegamites and aplites, Tertiary sediments of the Miocene, andesites, dacites and their tuffs, Pliocene deposits and Quaternary formations. Granites, pegmatites and aplites are imprinted in a series of crystalline shales, pegmatites appear in the form of hemispherical bodies, elongated lenses and stripes [4]. Andesite-Dacite tuffs formed in closed basins, they are related to the last phase of Dacite-Andesite magmatism in the torton: ash, lapil and other volcanic material was deposited over the sandstone.

The geological structure of the Zeolite tuff deposit "Toponica" consists of: lowland Miocene gray-blue clay sandstones, partly gray-green, then the horizon of white zeolite tuffs and upland Miocene sediments - clays, gravel, clay sand and gray-green sandy clay. The bottom sediments are built from gray-blue to gray-green sandstones. Zeolite tuff occurs in the form of a lens, which is interrupted in several places and intersected by cracks, where the thickness of the zeolite tuff is from 0.2 to 4.9 m.

3.2 Mineralogical and chemical analyzes of zeolite tuff

The tuff is white with yellow limonite scars on the surfaces of the cracks. It is crystalline in structure [6]. The examined tuffs show a pronounced zeolitization process and basically have a holocrystalline crystalline porphyry to vitrophyre texture, Figure 1.

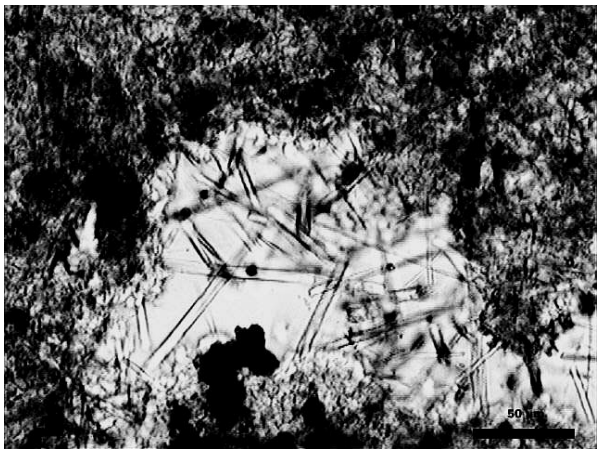

Figure 1. Elongated crystals of zeolite minerals in a zeolite tuff sample.

Clinoptilolite in sedimentary rocks mainly occurs in the form of euhedral plates, of several microns in length and thickness of 1-2μ [4]. The morphological forms of clinoptilolite presented in Figure 2 (ad) have characteristic monoclinic forms, with pronounced anhedral forms.

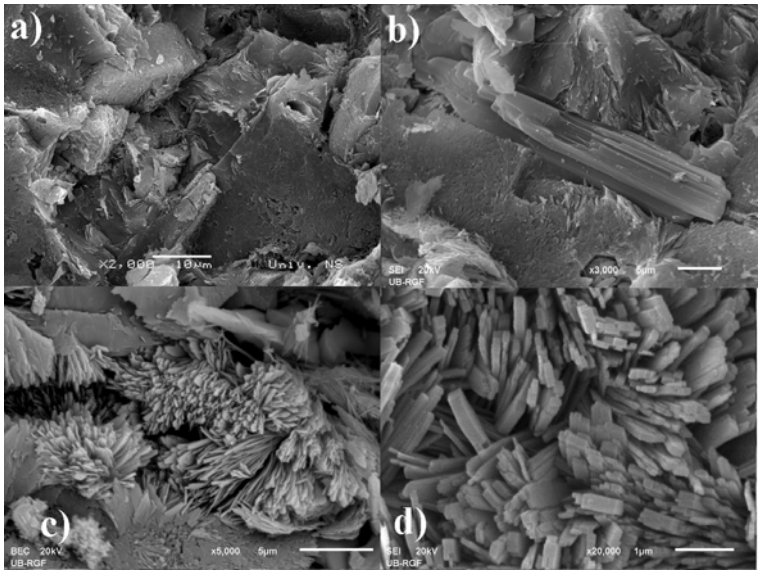

Figure 2. SEM micrographs of zeolite tuff.

Quantitative chemical analysis determined the chemical composition of the starting zeolite tuff, and is presented in Table 1. Atomic ratios (Si/Al), as well as the ratio of divalent and monovalent cations, were obtained based on quantitative chemical analysis. The cation exchange capacity of Zeolite tuff samples of Toponica (MmolM/ 100g) is 140 meq / 100g.

Table 1. Chemical composition of zeolite tuff of the Toponica deposit and ratio of present inorganic cations in hoylandites (two medium samples)

Oxide (%)	Trial 1	Trial 2	Sad.element (%)	Trial 1	Trial 2
SiO_2	67.5	60	Si	31.5	28.04
Al_2O_3	12	13.46	Al	6.3	7.1
Fe_2O_3	1	1	Fe	0.35	0.35
CaO	4.9	5.74	Ca	3.5	4.1
MgO	0.34	2.41	Mg	0.2	1.45
Na_2O	1.13	0.25	Na	0.83	0.18
K_2O	1.01	0.44	K	0.83	0.36
G. annealing	12.65	17	-	-	-
SiO_2/ Al_2O_3	5.62	4.46	Si / Al	5.00	3.95
$Na_2O/Na_2O + K_2O$	0.53	0.36	$Na^+/ Na^+ + K^+$	0.50	0.33
$CaO/CaO + MgO$	0.93	0.70	$Ca^{2+}/ Ca^{2+} + Mg^{2+}$	0.94	0.74

3.3 Structural analysis of Ca-clinoptilolite in zeolite tuff

The mineral composition of the tested sample of zeolite tuff from the Toponica deposit corresponds to microscopic examinations. The following are present in the sample: the mineral clinoptilolite, quartz, minerals of the mica group, minerals of feldspar (mainly plagioclase), Figure 3. Other minerals determined by the microscopic method were not detected because they are below the detection threshold.

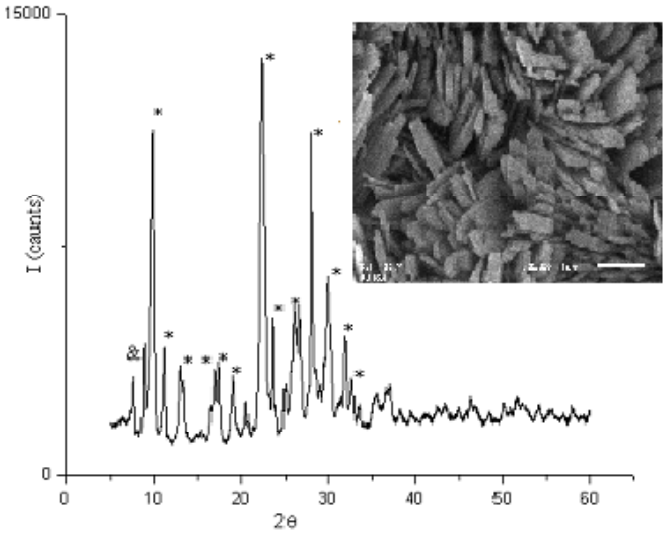

Figure 3 - X-ray diagram of clinoptilolite-Ca powder of zeolite tuff Toponica (symbol * represents the mineral clinoptilolite; symbol & represents a mineral from the mica group).

4. CONCLUSION

Based on the presented results, the zeolite tuff of the Toponica deposit contains a mineral from the heilanidite series, clinoptilolite, as the basic mineral component. The basic offline cation is calcium. The cation exchange capacity is 140 meq / 100g, which makes this mineral raw material extremely high quality and suitable for use in various industries.

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