University of Belgrade Technical Faculty Bor

### PROCEDINGS

### XXIII International Conference

# Ecological Truth

Editors Radoje V. Pantovic Zoran S. Marković

EcoIst 15

Hotel "PUTNIK", Kopaonik, SERBIA 17-20 June 2015

### UNIVERSITY OF BELGRADE TECHNICAL FACULTY BOR



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## Eco-Ist'15 PROCEEDINGS

**Edited by** 

Radoje V. PANTOVIC and Zoran S. MARKOVIC

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### GEOLOGICAL CHARACTERISTICS OF ZEOLITES FROM IGROS AS RAW MATERIALS FOR USE IN VARIOUS FIELDS OF ECOLOGY

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### **ABSTRACT**

Deposit of zeolitic tuff "Igroš" near Brus belongs to the village Igroš, which is administratively located in the area SO Brus and is about 3 km from the main road Krusevac - Brus. On the part of the field test site in Igroš the ore field "Igroš - Vidojevići", there are two ore bodies, "ore body I" and "ore body II ." In this paper are given the basic characteristics and presents of the results the latest research zeolitic tuff from deposits Igroš.

**Key words**: Igros, zeolitic tuff, clinoptilolite-heulandite group.

### INTRODUCTION

Zeolites are group of natural and artificial inorganic compounds, which have specific physicochemical properties appropriate for industrial application. These minerals make specific group of alumosilicates within tectosilicates because of their origin, chemical compositions, structural characteristics and application. Clinoptilolite-heulandite mineral series (HEU type zeolite framework) represents economically the main group of natural zeolites. Application fields are numerous: in ecosystems (organic sulphur disposal from industrial oils, air purification from SO<sub>2</sub>, CO<sub>2</sub>, caesium and strontium disposal from soils contaminated with nuclear waste, in agriculture, farriery [1].

Their physical properties are: gray-white to yellow colour with limonite skins which fill-up cracks and fractures. Mineralogical composition of the zeolitic tuffs are: QUARTZ, FELDSPARS, MICA, HEU-TYPE ZEOLITES, LIMONITE, CLAY MINERALS, VOCANIC GLASS, ZIRCON, APATITE, RUTILE

### GEOLOGICAL CHARACTERISTICS OF THE EXPLORATION AREA

The earliest Cretaceous sediments in the schist represent a high degree of metamorphism, mostly of sedimentary origin, transformed to amfibolitic facies. Diabase-chert formations (J2,3) was found at the south-western part of the terrain around Mosut, Igros and Sljivovo. Diabase and spilit ( $\beta\beta$ ) belong diabase-spilite-albitofirse formation. Neogene sediments were deposited in a complex tectonic depression known as the Moravian trench.

### RESULTS OF THE RECENT RESEARCH

By Geozavod-Geological Institute of Serbia in 1999 on the deposit of zeolitic tuffs "Igros" were conducted detailed geological research, in order to obtain data for the preparation of studies on reserves. For this purpose, the following works were done shooting and making situational plan in scale 1: 1,000, on an area of 2 hectares, making exploration wells, drilled 5 exploratory wells total piece 24.50 m. In 2008, the continued geological exploration at the mine field "Igros-Vidojevic" on ore bodies I and II [2].

### **Geological operations**

Geological research on the ore field "Igroš-Vidojevic" established two ore bodies, "ore body I" and " ore body II." By exploratory drilling completed in 2008 on two ore bodies have been dug 17 wells total meterage 299.0 m. Zeolitic tuff layer extends from the northwest to the southeast and can be monitored with interruptions over the length of 1.1 km.

Field mapping and exploitation works on the "ore body I" it was found that a layer of zeolitc tuff provides north-south direction and can be traced about 170 m along the strike and the decline in average about 50 m. Zeolitic tuff layer is interstratified in the Miocene-pliocene series shale green clay that make up the floor of clay and brown and green sandstones, which form the roof is. Zeolitic tuff layer is light gray to white colour average thickness of 1.64 m, with the general provision of the north-south and secondary statistical fall toward the north at an angle of about 4°.

Mapping the terrain in "ore body II" has been found that a layer of zeolitic tuff on the direction northwest-southeast and can be traced for a length of approximately 300 m and after the fall of about 100 m. Zeolitic tuff layer is interstratified in the Miocene-pliocene series of green clay, marl, shale brown clay that make up the floor of the conglomerate, shale brown clay and marl that make up the roof is. Zeolitic tuff layer is light gray to dark gray. By exploration drilling, investigating and recording notch open profile is determined zeolitic tuff layer with average thickness of 1.82 m, with the general provision of the north-south-southeast and secondary statistical drop in the northeast angle of 10°.

### Laboratory examinations

### Mineralogical and petrographical analyses

Deposits of zeolite tuffs are genetically related to volcano-sedimentary rocks. Tuffs rich in minerals HEU-type were created in marine and lacustrine sediments of the Senonian or Neogene age. The genesis of these zeolite tuffs related to the processes of diagenesis of volcanic glass. The mere lake environment had a significant impact on the formation and diagenesis minerals heulandite series. Grossly, mainly white to whitish yellow color, with frequent limonite scum. Mineralogical composition of zeolite tuffs test deposits is as follows: quartz, feldspar, mica, limonite - goethite, chlorites, volcanic glass, clay minerals, zeolite minerals, carbonate minerals group. As accessory minerals present are zircon, apatite and rutile.

Igros zeolite tuff deposit - The matrix of this tuff is hyalclastic with porous texture. Quartz grains are also well-preserved with typical angle-like forms and sharp edges. Feldspar minerals that are partially altered are mostly presented with plagioclase minerals. Zeolite minerals that are needle-like forms and very small dimensions are mainly distributed in matrix (up to  $10\mu$ ). Biotite is dominant mica mineral, which is primary, while muscovite (sericite) is mainly as secondary mineral. Biotite is partially altered. Products of its alterations are iron-oxides and hydroxides (mostly limonite and goethite). Accessory minerals, apatite and zircon are regularly breezy and without any marks of alteration. Presence of plant fossils is quite frequent.

- X-ray tests: A sample of zeolite was examined by X-ray powder diffraction (powder). In the analyzed sample showed the presence of the following minerals: zeolites clinoptilolite heulandite-type, quartz, feldspar, mica. The most common minerals are zeolite, and feldspar and quartz, far less present. Mica are present in the track. From feldspar minerals are dominantly represented plagioclase. Semiquantitative share of crystalline phases (minerals) is as follows: zeolites than 80%,  $\leq 10\%$  feldspar, quartz <10%. Advanced semiquantitative analysis was very difficult because the proportion of the amorphous (glassy) phase is relatively high. The diffraction pattern of the test sample is given in the appendix to the report [3], [4], [5]

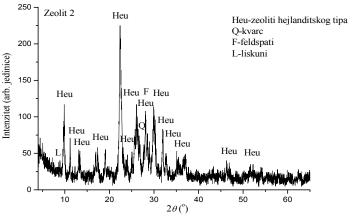


Figure 1. Diffractogram of zeolite powder sample Igroš

### Chemical analyses

Based on the determination of cation exchange capacity to "ore body I" values obtained indicate that there is only one variety of zeolitic tuff terminology defined as zeolitic tuff. The average value of cation exchange capacity of the zeolites in the "ore body I" amounts to  $166.9~\text{mEq}\/\/\/$  100 g.

Based on the analysis of the results of cation exchange capacity to "ore body II" observed two varieties of zeolite tuff: zeolitic tuff and tuff with zeolite. The average value of cation exchange capacity for zeolitic tuff is 137.85 meq / 100 g. The average value of cation exchange capacity for tuff with zeolite is 99.33 mEq / 100 g. According to the standards that are accepted in the "Institute for Technology of Nuclear and Other Mineral Raw Materials" from Belgrade, zeolitic tuff, that could be used (modified) for obtaining mineral adsorber mycotoxins as feed additive should have a value of cation exchange capacity  $\geq$ 130 mEq / 100 g.

The average value of cation exchange capacity of zeolitic tuff with "ore body I" and " ore body II is 152.38 meq / 100 g. The average cation exchange capacity of 152,38 meq / 100 g indicates the potentiality of separated layers zeolitic tuff as high-quality raw materials for obtaining mineral adsorber mycotoxins.

The quality of mineral resources zeolitic tuff "ore body I" is given in Tables 1-2.

**Table 1.** The silicate analysis samples of zeolitic tuff "ore body I"

| Elements     | SiO <sub>2</sub> | $Al_2O_3$ | FeO  | Fe <sub>2</sub> O <sub>3</sub> | CaO  | MgO  | TiO <sub>2</sub> | Na <sub>2</sub> O | K <sub>2</sub> O | $P_2O_5$ | G. Ž. |
|--------------|------------------|-----------|------|--------------------------------|------|------|------------------|-------------------|------------------|----------|-------|
| Content in % | 62,30            | 12,59     | 0,23 | 1,20                           | 4,08 | 1,94 | 0,22             | 0,70              | 0,63             | 0,016    | 15,65 |

- The average value of cation exchange capacity (KKI) amounted to 166.9 mEq / 100 g.
- clinoptilolite mineral content heulandite in tuff is approximately 90%.

**Table 2.** Content of heavy metal of samples zeolitic tuff "ore body I"

| Elements       | Co   | Cr  | Pb   | Zn   | Mn  | Sb   | Sn | Cd   | Cu   | Ti    | As   |
|----------------|------|-----|------|------|-----|------|----|------|------|-------|------|
| Content in ppm | 14,5 | 2,4 | 20,2 | 33,5 | 149 | 51,0 | 12 | 1,20 | 38,4 | 142,5 | 0,08 |

The quality of mineral resources "ore body II" is presented in Tables 3-5.

**Table 3.** Silicate analysis of samples zeolitic tuff "ore body II"

|              |                  | ,         |      |                                |      |      | 2                |                   |                  |          |       |
|--------------|------------------|-----------|------|--------------------------------|------|------|------------------|-------------------|------------------|----------|-------|
| Elements     | SiO <sub>2</sub> | $Al_2O_3$ | FeO  | Fe <sub>2</sub> O <sub>3</sub> | CaO  | MgO  | TiO <sub>2</sub> | Na <sub>2</sub> O | K <sub>2</sub> O | $P_2O_5$ | G. Ž. |
| Content in % | 62,23            | 13,06     | 2,63 |                                | 3,53 | 2,14 | 0,23             | 1,31              | 0,68             | 0,017    | 14,05 |

- The average value of cation exchange capacity (KKI) is 137.85 meg / 100 g.
- clinoptilolite mineral content hejlandite in tuff is approximately 85%.

Table 4. Table 2. Content Heavy metal in the samples zeolitic tuff "ore body II"

| Elements       | Co   | Cr   | Pb   | Zn   | Mn    | Sb | Sn   | Cd  | Cu   | Ti    | As  |
|----------------|------|------|------|------|-------|----|------|-----|------|-------|-----|
| Content in ppm | 13,6 | 24,2 | 20,2 | 43,1 | 107,8 | 45 | 12,5 | 1,1 | 24,7 | 123,9 | 0,2 |

**Table 5.** Silicate analysis of samples tuff zeolite "ore body II

|              | 0:0     | _         | •         |      |                   | _      | ~ =   | ~ ×   |
|--------------|---------|-----------|-----------|------|-------------------|--------|-------|-------|
| Elements     | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | CaO  | Na <sub>2</sub> O | $K_2O$ | G. Z. | G. Z. |
| Content in % | 63,67   | 12,72     | 3,38      | 2,43 | 1,93              | 1,27   | 3,90  | 8,13  |

- -The average value of cation exchange capacity (KKI) amounts to 99.33 meq / 100 g.
- clinoptilolite mineral content haulandite in tuff is approximately 50%.

### Technological examinations and field of application of zeolitic tuffs

Earlier long-term technological and industrial test the zeolitic tuff with same or comparable quality by experts ITNMS shown that it can be successfully applied in different fields of agriculture and the economy in general:

- micronized tuffs are added to a concentrated food for livestock and poultry, and in this way reduces the impact of toxic substances are present in an intensive cattle diet.
- production of organomineral fertilizers on pig farms, the absorption of ammonia from air and water by zeolitic tuff and tuff subsequent disposal of such arable land from the release of ammonia and enrichment of nitrogen,
- since zeolitic tuffs have the ability to absorb and release water, can be applied to the soil gravel composition of greater permeability, to prevent rapid drying of soil and leaching (relating) useful substances from the same.
- recultivation of degraded land-tailing example coal mines Stavalj near Sjenica is, by experts ITNMS has successfully rehabilitated by using zeolitic tuff,
- for cleaning the waste water, production of micronized materials and granulate based on zeolite tuffs,
- production of means for filtration and funds for environmental conditions, according to the patents of scientists of the Institute-ITNMS from Belgrade
- application in industry and special paper industry using fine abrasives and many other application areas.

### **CONCLUSION**

On the territory of the Republic of Serbia within the sedimentary deposits, there are several basins in which the isolated occurrences and deposits of zeolitic tuffs, which are economically very important mineral raw material. Tray of zeolitic tuff "Igroš"near Brus belongs to the village Igroš, which is administratively located in the area SO Brus and is about 3 km from the main road Krusevac - Brus.

Exploration drilling, exploratory digging and making exploitation floors is determined zeolitic tuff layer average thickness of 1.64 m, with the general provision of the north-south and secondary statistical fall toward the north at an angle of about 4 °. Mineralogical composition of zeolite tuffs test deposits is as follows: quartz, feldspar, mica, limonite - goethite, chlorites, volcanic glass, clay minerals, zeolite minerals, carbonate minerals group. As accessory minerals present are zircon, apatite and rutile.

In the deposit zeolitic tuff and tuff with zeolite "Igroš-Vidojevic" in two ore bodies I and II were established balance geological reserves of B + C1 categories of

zeolitic tuff and tuff with zeolite in the amount of 35,712 m3 or 50,817 t. The average value of cation exchange capacity of zeolitic tuff with "ore body I" and ore body II" is 152.38 meq / 100 g. The determined quality of mineral resources allows its use in different applications: for the production of micronized mineral supplement animal feed premixes and concentrates, then in the agricultural, plant production (slow acting fertilizers, reclamation of acid soils, improving water-physical properties of the soil, storage of seeds, fruits and vegetables), in virtually all industries (production of cosmetics industry beer and wine), and daily life (removal odors and filtering drinking water, etc.).

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