"Jablanica 1" – Prospective Zeolite Deposit

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The need for natural zeolite in Serbia is around 7000 t/year. Three deposits, located in the region of Krusevac, have reserves of about 2.2 million tons of zeolite, thus the prospective of this region is exceptional. The quality of zeolitized tuff is reflected in the high content of clinptilolite, which contributes to high market price of mineral raw material and its finished products.

Geologist of the company Contractor Ltd investigated three deposits of zeolitized tuffs on the slopes of Jastrebac mountain, of which the largest one, namely "Jablanica 1", was geologically explored in details.

Key words: Zeolitized tuffs, Zeolite, Jablanica 1, Clinoptilolite, Serbia

1. INTRODUCTION

On the western slopes of the Jastrebac mountain, near Krusevac, the geologists of the company CON-TRACTOR Ltd., have determined three deposits of zeolitized tuffs, the largest one of which, "Jablanica 1" was geologically explored in details. The totally identified reserves of deposits amounted to 1.613,000 t of dry ore. CONTRACTOR Ltd. owns over about 1/8 of the total reserves, ie 206.000 t. The deposit covers about 8 hectares and it represents a layer of zeolite, with the average thickness of about 18.5 m. The ore varies in quality, and consequently its application. It can be used in pharmacy, cosmetics, water protection, agriculture and remediation. During the investigation CONTRACTOR Ltd. Established that the selective exploitation of zeolite will give the maximum utilization of the deposit. The region of Krusevac is promising, according to rough estimates of CONTRACTOR's geologists, because these three deposits have resources of about 2.2 million tons of zeolite. Given that the need for natural zeolite in Serbia is around 7.000 t/year, prospective of this region is exceptional. The quality of zeolitized tuff is reflected in the high content of clinoptilolite, which contributes to high market price of mineral raw material and finished products.

2. DESCRIPTION OF THE DEPOSIT

"Jablanica 1" deposit is located in a micro-loca

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tion of the Jablanica village. The ore body is in the form of layer which extendes along the NW – SE direction, with a dippinig angle of $15-18^{\circ}$. Average thickness is 18.5 m, but the erosion of the top, partially destroyed the deposit. The layer has a constant thickness of about 18.5 m in deeper parts of the deposit.

Two varieties of tuff are distiguinshed in the deposit: white massive tuff and banded gray to dark gray sandy tuff. The bright white tuffs build the largest part of the deposit and they are in the upper layer, while the sandy tuffs are in the basal section [2].



Figure 1 - Geological cross-section trough the Jablanica 1 deposit

3. GENESIS OF THE DEPOSIT

In the basin of the river Rasina during the middle Miocene, the volcanic ash, mostly composed of glass mass was deposited. Sedimentary zeolite is formed by diagenetic changes of volcanic glass in lacustrine environments [1]. The formation of "Jablanica 1" deposit is thus related to Neogene explosive volcanism of dacite composition, and diagenesis of pyroclastic rocks in a freshwater lake [8]. Fragments of tiny grains of quartz, feldspar and mica were also registered.

4. GEOMECHANICAL CHARACTERISTIC OF THE DEPOSIT [1]

Geomechanical characteristics of the deposit were tested for optimal choice of mining machinery, which will perform exploitation.

Geomechanical parameters of the working environment were examined on test bodies obtained from core samples from drill holes and the exploration benches. The test results are shown in Table 1.

In order to check the geological structure of the limited part of the deposit, shape and position of the ore layer and the quality of zeolitized tuff two boreholes were drilled in 2006.

Basic information about boreholes that were performed in the whole deposit, are shown in Table 2. Borehole marks are confedential, for this reason they are not given in the tables

Table 1. Geomechanical parameters of the zeolite tuff of the certified reserves

5			
Parameter	No. of tests	Min-max values	Mean values
bulk density $\gamma_v(kN/m^3)$	5	13,82- 19,22	16,52
specific gravity γ (kN/m ³)	1	21,18	21,18
porosity n (%)	1	42,45	40,47
coeff. of porosity e	1	0,680	0,680
uniaxial compressive strength σ (daN/cm ²)	5	172,16- 252,84	207,16
tensile strength σ_z (daN/cm²)	5	20,21- 25,93	23,66
cohesion C (daN/cm ²)	1	33,6	33,6
internal friction ϕ (°)	1	31° 23'	31° 23'
velocity of longitudinal waves $V_p \left(m/s \right)$	5	1973-2141	2077
velocity of transversal waves $V_s (m/s)$	5	811-1070	956
dinam. modulus of elasticity. $E_{din} (GN\!/\!m^2)$	5	2,53-4,20	3,45
Poisson coeff. µ _{din}	5	0,33-0,40	0,36

Table 2. Basic information on exploration boreholes of the whole "Jablanica 1" deposit

No.	Borehole elevation (m a.s.l)	Drilling depth (m)	Obtained core (%)	Ore thickness (m)
1.	235,10	31.0	87,74	9.8
2.	238,00	44.5	83,82	18.5
3.	246,60	40.0	88,25	7.5
4.	272,90	29.0	74,36	7.8
5.	279,15	16.6	79,52	13.5
6.	287,90	26.0	84,61	19.2
7.	273,30	34.7	70,60	19.5
8.	259,60	28.5	69,47	17.0
9.	265,70	19.0	90,52	18.0
10.	276,80	26.5	83,02	17.8
11.	260,20	35.0	85,14	15.5
12.	254,99	23.4	94,87	19.3
13.	261,32	21.1	96,68	13.6

Table 3. Basic information on two exploration boreholes of "Jablanica 1" deposit (2006)

No.	Borehole elevation (m a.s.l)	Drilling depth (m)	Obtained core (%)	Ore thickness (m)
1.	251,99	27.5	93.00	18.5
2.	261,16	21.5	97.80	19.0

5. BASIC INFORMATION ABOUT THE DEPOSIT

Physical and mechanical properties [6]

Bulk density all together with pores and cracks in the natural wet state is 1.41 to 1.96 g/cm^3 . Bulk density in the dry state together with pores and cracks is 1.243 g/cm^3 . The specific weight with the pores is 2.16 g/cm^3 . Average porosity is 42.45%.

Chemical characteristics [9]

Determination of the zeolitized tuffs' chemical composition in the "Jablanica 1" deposit was done by making partial and complete analysis of indi vidual and composite sample.

Chemical analysis of individual and composite sample were performed by classical methods, as well as atomic absorption spectroscopy. Percentage of oxides was obtained by stoichiometric calculations. In the first stage of the research complete chemical analysis were carried out. We examined several representative samples of white and gray tuff, and mixtures thereof, obtained by sampling several old excavations. In order to control the previous results, in 2006, two old mining operations were tested (R -1 and R-2).

The results are shown in Table 3.

Complete analysis of individual samples of white and gray tuff from the surface indicate some differrences in the chemical composition of zeolite.

During 2006, ten individual samples from boreholes were tested (Table 5).

Table 4. Chemical com	position (in %)) of individual	samples of white	e and grav zeol	ite (2006)

Tuff variety	1	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O
white	1.	62,47	13,03	2,90	2,80	2,81	1,43	3,84
white	2.	60,79	12,42	2,22	3,60	2,01	1,68	1,80
white	3.	62,20	13,98	4,22	3,11	2,42	-	-
white	4.	62,22	9,63	4,87	4,42	1,59	-	-
white	5.	59,01	12,27	3,52	2,66	2,07	0,12	0,76
C _{sr}	6.	61,34	12,27	3,55	3,32	2,18	1,08	2,13
gray	7.	61,50	12,38	2,37	3,49	1,99	-	-
gray	8.	62,14	11,58	2,37	2,42	3,66	-	-
gray	9.	59,50	11,80	3,20	2,80	1,84	0,05	0,96
C_{sr}	10.	61,05	11,92	2,65	2,90	2,50	0,05	0,96

Commla monte	Chemical	Chemical composition of individual samples (%)							
Sample mark	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O		
P-1	65,0	13,32	1,52	3,15	1,73	0,77	2,28		
P-2	64,0	12,56	1,23	3,18	1,76	0,43	2,29		
P-3	63,0	12,65	1,12	3,36	2,02	0,28	2,34		
P-4	57,0	11,52	1,19	7,14	1,74	0,29	2,21		
P-5	61,0	12,58	1,24	4,20	1,72	0,46	2,31		
P-6	64,0	12,18	1,37	3,01	1,63	0,48	2,11		
P-7	65,0	11,71	1,16	3,08	1,47	0,43	2,15		
P-8	61,0	12,57	1,27	3,15	2,06	0,57	2,64		
P-9	64,0	13,33	1,42	3,64	1,72	0,67	2,36		
P-10	59,0	13,13	1,47	5,32	1,82	0,37	2,13		
Csr	62,3	12,55	1,23	3,92	1,77	0,47	2,28		

Table 5. Chemical composition of individual samples from boreholes, 2006

Table 6. Chemical composition (in %) of composite samples from boreholes, 2006

No.	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O
1	63,13	12,19	3,31	3,92	1,73	0,77	4,00
2	60,26	13,70	3,30	3,92	1,76	0,43	4,20
3	62,47	13,03	2,90	2,80	2,02	0,28	3,84
4	62,37	12,06	2,90	3,36	1,74	0,29	5,50
5	63,29	13,42	2,90	3,36	1,72	0,46	2,53
6	67,75	14,00	2,07	3,36	1,63	0,48	1,76
7	63,04	13,41	2,74	5,20	1,47	0,43	2,38
8	64,82	14,46	2,07	3,15	2,06	0,57	1,87
9	65,14	14,30	2,90	3,64	1,72	0,67	1,59
10	64,96	14,85	2,70	5,32	1,82	0,37	1,00
11	64,77	14,23	2,07	3,36	4,23	0,10	0,81
12	64,75	12,49	3,31	2,80	3,12	0,91	3,20
13	62,21	13,60	2,90	2,80	3,42	0,61	3,16
C _{sr} 1964	63,77	13,52	2,77	3,47	2,42	0,95	2,76
14	61,30	12,37	1,37	4,69	1,83	0,54	2,30
15	63,50	12,75	1,32	3,64	1,71	0,63	2,31
C _{sr} 2006	62,40	12,56	1,34	4,16	1,75	0,58	2,30

C_{sr} 2006

Csr deposit

Chemical analysis of individual samples from boreholes performed in 2006 indicates the uniformity of the chemical composition.

15 composite samples obtained from the core of boreholes in 2006 were tested, which were formed from material of whole ore interval. The test results are shown in Table 6.

The results of complete chemical analysis of composite samples from boreholes indicate that between average chemical composition of tuff established in 1964 and 2006, there were no significant differences.

The differences in the contents of the individual chemical components, such as in K_2O , a minor deviations are within the limits of permissible error for the applied analytical methods, which is of great importance for the evaluation of the results presented because it provides values of average chemical composition of the entire deposit of 1.612 Mt zeolitized tuff (Table 7).

K₂O 2,76

2,30

2,70

-	-					
Average content	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O
C _{sr} 1964	63,77	13,52	2,77	3,47	2,42	0,95

1.34

2,58

Table 7. Average chemical composition (in %) of composite samples

12.56

13,39

The results of chemical analysis confirmed that the tuffs from "Jablanica 1", for its chemical properties, may represent the zeolite raw material with the dominant mineral clinotpilolite.

62,40

63,58

Mineralogical and petrographic studies

Mineralogical and petrographic studies were performed at the Institute for Refractory Materials, Kraljevo. By microscopic examination, all samples are determined as tuff of pyroclastic structure, made up of tiny fragments and core mass. They have a massive texture. The primary mass of tuff, as a major component (70 - 95%), is completely altered volcanic glass. It is built of very fine-grained cryptocristalline, poorly - anisotropic aggregate which is difficult to determine by optical methods. The emergence of crypto - crystalline aggregates is twofold, the largest amount is in the weight of tuff, where the grain size of 3 - 10 nm dominates, while the other type fills certain cavities and constructs slightly larger aggregate. Fragments are quartz, feldspar and mica. Rare fractured quartz grains are sometimes bipyramidal, feldspar grains in fragmented angular shape sizes up to 0.3 mm are sometimes caught in the process of alteration. Fresher plagioclase grains (30 - 35% An) are characterized by polisynthetic lamellae or zonal structure. Among femic ingredients, partially chloritized biotite is dominant, and much less present are amphiboles (pyroxene - augite). The basic mass has the same minerals of finer grain and vitreous mass.

Based on the results of microscopic tests and chemical composition, tested rock is defined as finegrained diagenetic altered dacite tuff from heulandite group with clinoptilolite as a dominant mineral.

X-ray analysis [10]

X-ray analysis were performed on a total of 23 samples (1964) and 10 samples (2006). The domi-

nant phase in the investigated tuffs is zeolite from heulandite/clinoptilolite group. Mica, quartz, amphibole and calcite are present in minor scale. Identical results were obtained in two stages of testing 1964/2006.

0.58

0,91

1.75

2,33

Tests were performed using a diffractometer Philips type PW 1009 CoK radiation, Fe - filter at the goniometer speed of $1^{\circ}/20$ min, at a speed of paper 400 mm/h, Rc = 2, we used slits $1^{\circ}-0.1^{\circ}$ mm/ 1° .

DT and TG analyzes [5]

4.16

3,56

The tests were carried out in 2006 on the same samples in which the X-ray analyzes were performed. Differential thermal analysis of zeolitized tuff was performed using Adamel ADT 76, with a sensitivity of 0.1 mV. In the diagrams to a temperature of 350°C there are two endothermic effect, which correspond to the zeolite clinoptilolite/heulandite. In some samples endothermic effects in the interval of 700-950°C with a peak at 890°C indicate the presence of calcite.

Thermogravimetric analysis was conducted on a STANTON termal scale with a heating rate of 10% for 1 min in the range of 1000°C. TG tuff tests show uniform mass loss of 9.19 to 12.05% up to 500°C. Mass loss corresponds to dehydration of zeolitic water. The total mass loss up to a temperature of 1000°C is slightly higher and amounts from 9.96 to 16.02%. The difference in weight loss between 500 and 1000°C is 1 - 1,5% and is caused by the destruction of the crystal lattice of the zeolite, and values to 3.97% correspond to CO_2 emissions, ie dissolution of calcite.

Sorption capacity [7]

Sorption capacity tests were performed on samples of white tuff and the results show that the adsorption sensitivity of zeolite is extremely high, especially in the first two hours. Based on the adsorption capacity, zeolite from "Jablanica 1" deposit is classified as high-quality adsorbent. In particular, zeolite has a high adsorption of substances at low concentrations.

Table 8. Test results of natural zeolite's sorption capacity

Parameter	Unit	Result
may C	meq u NH ₃ /g	1,51
max C _{NH3}	mg NH ₃ /g	25,74
max C _{etanol}	%	7,58
max C _{H2O}	%	12,87

Adsorption tests of engine oil SAE 15-40, euro diesel, heating oil and gasoline were carried out in order to implement zeolite to petrol stations, for rapid intervention in the sorption of hazardous liquids. The tests have given excellent results.

Cation exchange capacity [7]

Cation exchange capacity was performed in three independent laboratories that operate with various methodologies and standards, and the conclusion is given only on the basis of test results of composite samples, where CEC values of zeolitized tuff varies from 146 to 191 meq/100 g. Comparing the results of CEC values of zeolite from ,Jablanica 1" deposit with the results of zeolite from Igroš deposit (140-160 meq/100g) and from Zlatokop deposit (150-196 meq/100g), it can be concluded that the CEC values of the ,Jablanica 1" deposit are larger than Igroš and approximately the same as in Zlatokop near Vranje [3],[4].

Table 9. Cation exchange capacity of two composite samples

Sample mark	Ca	Mg	Na	K	CEC
K-I	121	20,4	4,5	45,1	191 meq/100g
K-II	86	16,1	4,0	40,0	146 meq/100g

6. DETAILED INFORMATION ON VERIFIED RESERVES IN ONE PART OF THE DEPOSIT "JABLANICA 1"

Identified geological resources in the zeolitized tuff "Jablanica 1" deposit amounts to 1.63 million t of dry ore. Balanced reserves of zeolite are in an amount of 206 000 t of dry ore, which is 1/8 of the total reserves of the deposit, and the deposit was investigated by the CONTRACTOR Ltd. Ripanj – Beograd.

The Republican Commission for certifying reserves reviewed all test results and as a medium of average values determined the following:

Average mineral composition: Ca-clinoptilolite (min. 75%), mica (15%), and calcite + quartz + feldspar + amphibole ($\approx 10\%$).

Table 10. Average chemical composition of zeolitized tuff

Parameter	Results	Parameter	Results
SiO ₂	63,58	H ₂ O	3,81
Al ₂ O ₃	13,39	LOI	10,15
Fe ₂ O ₃	2,58	Cr	38 ppm
CaO	3,56	Co	37 ppm
MgO	2,33	Pb	51 ppm
Na ₂ O	0,91	Zn	66 ppm
K ₂ O	2,70	Cu	10 ppm
TiO ₂	0,07	As	35 pppm
MnO	0,09	Cd	88 ppm
SO ₃	0,13	Sr	450 ppm
P ₂ O ₅	0,21	Ва	550 ppm

Table 11. Physical and mechanical characteristics of zeolitized tuff

Parameter	Mean value
density with natural moisture	1,596 g/cm ³
dry state density	$1,243 \text{ g/cm}^3$
specific mass	2,160g/cm ³
porosity	42,45%
water apsorbing	28,38%
Mohs scale of mineral hardness	3-3,5
specific active surface	142 m ² /g
natural radioactivity: ΣU	8,93 Bk/kg
²²⁶ Ra	8,07
²³² Th	56,19
⁴⁰ K	258,6
g-index	<1,0
artificial radioactivity: 137Cs	<0,4 Bk/kg

Table 12. Ion exchange and adsorption properties of zeolitized tuff

Parameter	Mean value
CEC	168 meq/100g
max C _{NH3}	25,74 mgNH ₃ /g
max C _{etanol}	7,58%
max C _{H2O}	12,87%

7. EXPLOITATION OF ZEOLITE

Exploitation of ore is performed by universal mining machine with loading the zeolite in the truck. Excavation is performed on benches of 3 m or even less depending on the quality of the zeolite in the layer. The working angle of the benches is 65° , while

hauling is done over benches to the lowest bench of the floor of the deposit.

If necessary, in the course of work will be used bulldozer with a ripper as additional operating element, which disintegrates mineral mass.

Excavated zeolite is transported to the landfill, which is located at 3.5 km from the tray, on the regional road Krusevac - Pristina. The raw material is stocked at the place designated for commercial landfill, which is a temporary mining landfill. The raw material is then loaded on trucks and transported to the company in Ripanj, where further processing will be performed.

8. CONCLUSION

Rasina basin, on the slope of Jastrebac and Kopaonik mountains, presents a large potential for development of exploitation and processing of zeolite. Verified quality of zeolite in the "Jablanica 1" deposit will enable the start of a new industry.

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REZIME

JABLANICA 1 – PERSPEKTIVNO LEŽIŠTE ZEOLITA

Potrebe Srbije za prirodnim zeolitom su oko 7000 t/god. Tri ležišta, koja se nalaze u Kruševačkom regionu, imaju rezerve zeolita od oko 2,2 miliona tona, stoga je perspektiva ovog regiona izuzetna. Kvalitet zeolitiziranog tufa se ogleda u visokom sadržaju klinoptilolita što mineralnoj sirovini i gotovim proizvodima, daje visoku tržišnu cenu.

Geolozi kompanije Contractor d.o.o. su istražili tri ležišta zeolitiziranih tufova na obroncima planine Jastrebac, od kojih je najveće, "Jablanica 1", detaljno geološki istraženo.

Ključne reči: zeolitizirani tufovi, zeolit, Jablanica 1, klinoptilolit, Srbija