Sedimentary Zeolite Deposits in Slovakia

● **Exploited deposit**

● **Potential resources**

1. NIŽNÝ HRABOVEC
2. MAJEROVCE
3. KUČÍN
4. VEĽKÁ TŔŇA
5. BYŠTA
6. BARTOŠOVA LEHÔTKA – PASEKA
7. SKLENÉ TEPLICE

Zeolite occurring ubiquitously in exploited and unexploited deposits is *clinoptilolite*. *Mordenite* is also largely present at **Veľká Tŕňa** and **Byšta.**
This report is limited to the presently exploited formations.

NIŽNÝ HRABOVEC – MAJEROVCE – KUČÍN FORMATIONS

Zeolite occurrence: Clinoptilolite-rich tuff

Geology: The Eastern Slovakian basin with its basement of graben-synclinal structure was filled by Neogene clastic sediments, volcanogenic rocks and evaporites. The total thickness of the Neogene sequence reaches 7000 m. Diverse lithofacies were affected by volcanic activities of acidic to intermediate character, which continued during the whole Miocene period. Clay minerals and zeolites occur as the major or minor constituents of tuffs in the all Miocene stratigraphic stages (1-3). Zeolitization of stratiform character, showing vertical mineralogical zoning, constructed by clinoptilolite and analcime is associated exclusively with the bedded marine Lower Badenian sequence of rhyodacitic volcanoclastics, the so-called **Hrabovec tuffs** (1, 4).

Mineralogy: It is characterized by stable occurrence of clinoptilolite (mostly K,Ca-rich, e.g., in the Nižný Hrabovec occurrences), in association with low cristobalite, both as a result of silica glass alteration. Original pyrogenic minerals in the tuffs do not exceed 20% including quartz, plagioclases and sporadically chloritized biotite (5-7). Clinoptilolite content, regularly checked by X-ray diffractometry and other techniques, ranges between 50 and 90% throughout the deposit.

Aerial view of the Nizný Hrabovec deposit

A representative rock composition is as follows:

Phase	%
Clinoptilolite	84
Low cristobalite	8
Quartz	traces
Felspar	4
Illite	4
Carbonate (calcite)	<0.5

Chemistry:

Clinoptilolite-bearing tuff

Chemical composition

The following table reports the chemical composition of representative samples of clinoptilolite-bearing tuffs (wt. %)

Oxide	Nižný Hrabovec	Majerovce	Kučín
SiO_2	66.97	69.40	67.07
Al_2O_3	10.61	11.62	11.31
TiO_2	0.24	0.13	0.20
Fe_2O_3	1.72	1.28	1.45
MnO	0.03	0.01	0.02
CaO	2.90	2.78	2.91
MgO	0.73	0.90	0.99
K_2O	2.96	2.82	2.73
Na_2O	0.68	0.34	0.80
H_2O	12.90	10.72	12.40

Cation exchange capacity The cation exchange capacity (CEC), estimated according to ČSN 72 1076 Czech National Standard, based on cation displacement by a NH_4^+ solution, ranges from 1.2 to 1.5 equiv./kg.

Clinoptilolite

Chemical formula The crystal chemical formula of clinoptilolite from a representative Nižný Hrabovec sample is:

$|(Na_{0.21}K_{1.74})\ (Ca_{1.71}Mg_{0.31})\ (H_2O)_{18.28}|\ [Al_{6.11}\ Si_{29.90}O_{72}]$.

Crystallography The unit cell parameters of clinoptilolite from Nižný Hrabovec are as follows:

a [Å]	b [Å]	c [Å]	β [°]	V [Å^3]
17.79(2)	17.99(2)	7.43(1)	116.5(1)	2132 (4)

Physical and mechanical properties:

Appearance (colour)	gray-green
Compressive Strength	33-41 MPa
Rock porosity	24-32%
Effective pore diameter	0.4 nm
Density	2200-2440 kg/m^3
Bulk density	1600-1800 kg/m^3
Thermal stability	400°C

Reserves and production: Estimated zeolite reserves are in the order of 9,500,000 tons. Annual production capacity is roughly 200,000 tons with reference to ground zeolites and 20,000 tons as regards granular zeolites.

Main applications: The main fields of use of Nižný Hrabovec material are::

(a) Agriculture Covers some 70-80% of zeolite production, especially in the following areas:
soil additive**;**
crop protection**;**
constituent of three-component mineral fertilizers;
component of feeding mixtures for animals**;**
litter additive (8-14)**.**

(b) Industry and environment Wastewater, sewage and drinking water purification;
dust and flue gas cleaning;
filler in several industrial products (rubber, paper, wood).

(c) Construction Component of cement and concrete composites (15-19);
geosynthetic clay liner (20, 21).

References

1. Rudinec, R. (1978): Paleogeographical, lithofacial and tectonogenetic development of the Neogene in Eastern Slovakia and its relationship to volcanism and deep tectonics. *Geologica Carpathica*, **29** (2), 225–240.
2. Šamajová, E., Kraus, I. (1985): Distribution of smectites and zeolites in the West Carpathians. In Proc. 5th Meeting of European Clay Groups, Charles University, Prague, p. 321–328.
3. Reed, J.K., Gibbson, M., Jr., Vass, D. (1993): Hydrocarbon potential of sandstone reservoirs in the East Slovakian Basin, Part 2: Zeolites and clay minerals. *Journal of Petrological Geology*, **16**, (2) 223–236.
4. Šamajová, E., Kraus, I. (1976): Manifestations of zeolitization in neovolcanics of Slovakia. In Proc. 7th Conf. on Clay Minerals and Petrology, Karlovy Vary, Charles University, Prague, p. 391–399.
5. Varga, I. (1984): The first zeolite deposit in Czechoslovakia: results of geological exploration of the clinoptilolite tuff in Nižný Hrabovec. *Mineralia Slovaca*, **16** (4), 371–376 (in Slovak).
6. Kozáč, J., Očenáš, D., Derco, J., Rusnák, D. (1981): Nižný Hrabovec – zeolitic tuffs – applied technological research. Manuscript, Geofond, Bratislava, 224 p. (in Slovak).
7. Varga, I. (1988): Economic geological classification of zeolite occurrences in Slovakia. *Mineralia Slovaca,* **20** (3), 249-259 (in Slovak).
8. Olver, M.D. (1997): Effect of feeding clinoptilolite (zeolite) on the performance of three strains of laying hens. *British Poultry Science,* **38** (1), 220–222.
9. Parlat, S.S., Yildiz, A.O., Oguz, H. (1999): Effect of clinoptilolite on performance of Japanese quail (*Coturnix coturnix japonica*) during experimental aflatoxicosis. *British Poultry Science*, **40** (2), 495–500.
10. Ortatatli M., Oguz H. (2001): Ameliorative effects of dietary clinoptilolite on pathological changes in broiler chickens during aflatoxicosis. *Research in Veterinary Science*, **71** (1), 59–66.

11. Meisinger, J.J., Lefcourt, A.M., Van Kessel, J.A., Wilkerson, V. (2002): Managing ammonia emissions from dairy cows by amending slurry alum or zeolite or by diet modification. *Scientific World Journal*, **27** (6), 860–865.
12. Melenová, L., Ciahotny, K., Jirglová, H., Kusa, H., Růžek, P. (2003): Removal of ammonia from waste gas by means of adsorption on zeolites and their subsequent use in agriculture. *Chemické Listy*, **97** (4), 562–568 (in Czech).
13. Rizzi L., Simioli M., Roncada P., Zaghini A. (2003): Aflatoxin B1 and clinoptilolite in feed for laying hens: effects on egg quality, mycotoxin residues in livers, and hepatic mixed-function oxygenase activities. *Journal of Food Protection*, **66** (6), 860–865.
14. Papaioannou, D.S., Kyriakis, C.S., Alexopoulos, C., Tzika, E.D., Polizopoulou, Z.S., Kyriakis, S.C. (2004): A field study on the effect of dietary use of a clinoptilolite-rich tuff, alone or in combination with certain antimicrobials on the health status and performance of weaned, growing and finishing pigs. *Research in Veterinary Science*, **76** (1), 19–29.
15. Janotka, I., Špaček, A., Jeřábek, M. (1992): Aplikácia cementovej suspenzie so zvýšenou chemickou odolnosťou (Application of cement suspension of increased chemical resistance), *Stavebnícky časopis (Building Research Journal)*, **40**, 681–697.(in Slovak).
16. *ZEOFIX* ® (1998): *(*firm folder), Zakládaní staveb, a.s., Prague (Czech Republic) (in Czech).
17. Janotka, I., Krajči, Ľ. (2000): Utilization of natural zeolite in Portland pozzolan cement of increased sulfate resistance, In Proc. 5th CANMET/ACI Conference on Durability of Concrete, Vol. I, Barcelona (Spain), p. 223-238.
18. Janotka, I., Ray, A., Mojumdar, S.C. (2004): Acid and sulfate resistance of Portland cement - natural zeolite mortar, In Proc 8th CANMET/ACI International Conference on Fly Ash, Silica Fume, Slag and Natural Pozzolans in Concrete, Las Vegas, p. 639–652.
19. Janotka, I., Nürnbergerová, T., Križma, M., Bágeľ, Ľ. (2006): Mikrostruktura i właściwośti betonu zawierajacego cement z dodatkiem 15% naturalnego zeolitu (Structure – property study of concrete containing cement blended with 15 percent of natural zeolite). *Cement Wapno Beton,* Vol.XI/LXXIII (3),.159-170 (in Polish and English).
20. Janotka, I., Kišš, Š, Baslík, R. (2002): Geosynthetic mat Tatrabent – development, production and application, *Applied Clay Science*, **21**, 21–31.
21. Janotka, I., Kišš, Š., Svoboda, I., Novotný, J. (2000): Utilization of GCL at recultivation works of burning dump of mine Kateřina, Radvanice, In Proc. 2nd European Geosynthetics Conference and Exhibition, Vol. 2, Bologna, p. 733 – 735.

This issue is based on a review article by M. Vatalová, M. Vida, E. Šamajová and I. Janotka. Further information on exploited and unexploited deposits is available from Professor Ivan Janotka (Ivan.Janotka@savba.sk).