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Usage of zeolite raw materials as natural barrier for conservation of nuclear waste

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Abstract

The presence of manganese oxides and hydroxides forming thin crusts up to 4-5 mm thick, deposits and impregnations with black color was found in the pink-reddish clinoptilolite zeolites from the field works in the area of the Most deposit, Bulgaria. The aim of the present research is to study the zeolite raw material in the area of the deposit in order to determine the manganese mineralization. The presence of certain microporous minerals, referred to as octahedral molecular sieves (OMS) and octahedral layered materials (OL) will increase the value of the zeolite raw material from the deposit in order to use them as a sorbent of heavy metals and radionuclides to solve some ecological problems.

Keywords: *Zeolite, Cryptomelane, OMS, OL, Waste*

Rezumat. Utlizarea materiei brute de zeolit ca barieră naturală pentru consevarea deșeurilor nucleare. Prezența oxizilor și hidroxilor de mangan ce formează cruste cu grosimi de până la 4-5 mm, depozite și impregații de culoare neagră au fost semnalate în cadrul depozitelor de zeolit clinoptilolit de culoare roz-roșiatică în timpul lucrărilor de teren din apropierea depozitului Most din Bulgaria. Lucrarea de față studiază zeolitul ca materie primă din zona de origine a depozitului pentru a determina mineralizația de mangan. Prezența anumitor minerale miroporoase, denumite site moleculare octaedrice (OMS) și materiale în straturi octaedrice (OL), va crește valorea materiei prime de zeolit, permițând folosirea acestuia ca absorbant pentru metalele grele și nuclid radioactiv, rezolvând astfel unele probleme de natură ecologică.

Cuvinte-cheie: *zeolit, criptomelan, OMS, OL, deșeu*

Introduction

Nuclear power plants produce highly radioactive waste through the nuclear fission of uranium and plutonium or the fusion of hydrogen with helium. The decomposition of this waste poses a great danger to humans, animals and plants for millennia, so it must be well stored and isolated. Nuclear power plants have been in operation for more than 50 years, but up to date there is no reliable method for storing high-level radioactive waste (Nikolova & Nikishanliev, 2015). The big deposits of zeolite and bentonite near the town of Kardzhali (Bulgaria), their low self-value and their unique ion exchange and adsorption properties, make them attractive for purification of wastewater from ions of heavy metals (Kovacheva-Ninova et al., 2002). Zeolite exchangeable ions are relatively harmless and makes them attractive native materials for removing undesirable heavy metal ions from industrial and processing effluent water. In addition, zeolite loaded with heavy metal ions can be easily regenerated (Nikolova et al., 2002).

Deposits and occurrences of zeolites are established in the vicinity of the villages Most, Perperek (Southern Bulgaria), and Lyaskovets (Central-northern Bulgaria). They have Oligocene age and were formed in marine environment. On the basis of accomplished exploration works the proved reserves in these deposits (contoured by common ion exchange and sorption capacity) are more than 500Mt (Brunkin & Boyadzhiev., 1980, Brunkin et.al. 1983). Natural zeolite added to soil improves its agrochemical and ecological characteristics. As a result of a study conducted with zeolites from the city of Kardzhali (Katsarova et al., 2021), it was established that natural zeolite, as an environmentally pure material, can be used to increase yield, reduce agricultural costs and protect natural soil resources .

Natural zeolites applied together with mineral fertilizers on contaminated soils with Cd>Zn>Cu>Pb significantly improve the quality of agricultural crops compared to the sanitary standards for safety in the Republic of Bulgaria (Dinev et al., 2021).

For the purposes of the present study, the Most deposit was tested. It is located in the Northeastern Rhodopes (Figure 1). Manganese oxide mineralization, a natural raw material combining different types of microporous minerals, has been determined, in view of their potential application for solving various ecological problems. Manganese mineralization has so far not been studied by other authors.

Materials and methods

To determine manganese mineralization, diffractometric X-ray analyses and microscopic scan were performed. This research was made for determine the composition, structural and optical characteristics of the minerals and the microstructural features of the rocks from tested manifestations. Special samples of zeolite rocks containing manganese oxide mineralization were studied (Figure 2). Polarization microscopes POLAM - R-311 and NU – 2 in Department of GPPI, University of Mining and Geology "St. Ivan Rilski", Sofia are used.

With the help of scanning electron microscope SEM - JEOL JSM-6301F (110) at Chalmers University of Technology, Department of Radio and Space Science, Gothenburg, Sweden the morphology of zeolite minerals were studied.

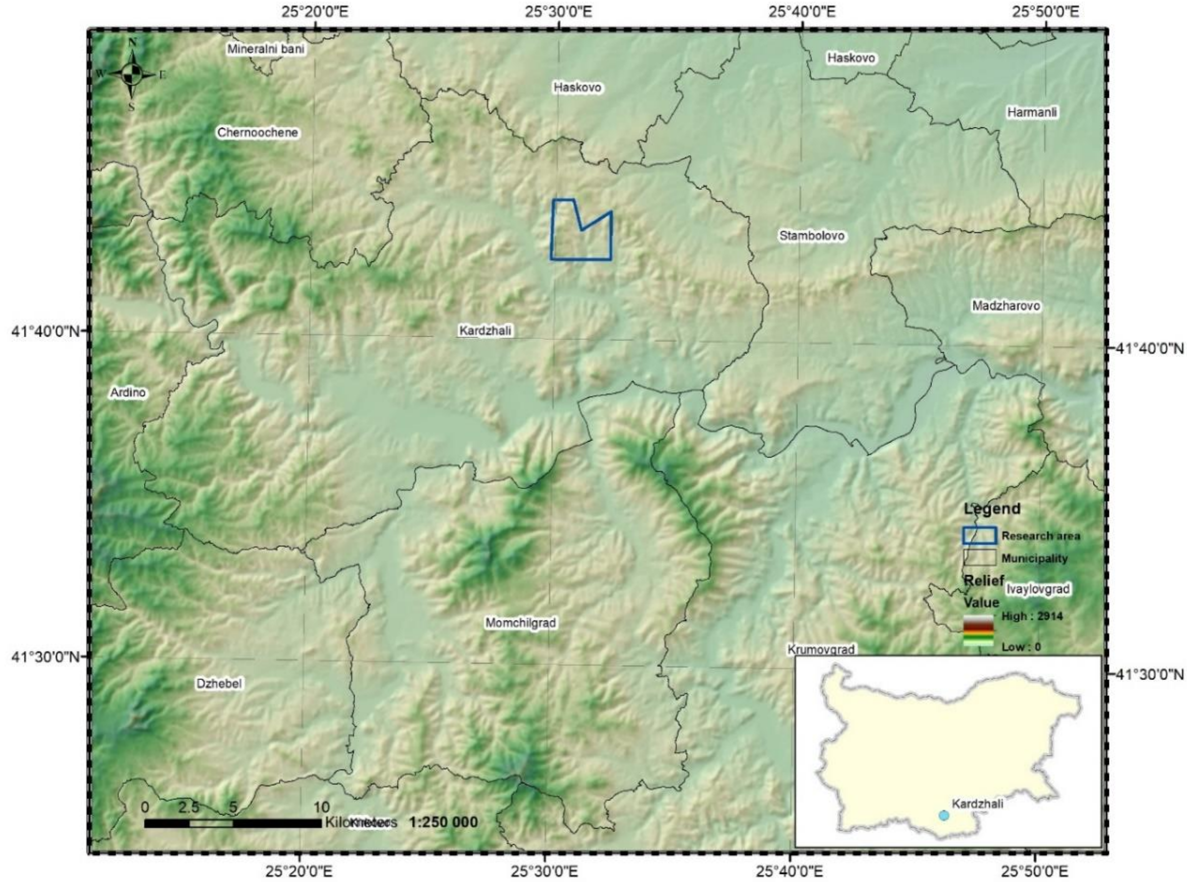

Fig. 1: Shaded relief map of the Northeastern Rhodopes. Political boundaries are shown by black lines. Inset map shows the location of the larger map with reference to Bulgaria. The blue box indicates the boundary of the studied area

Geological framework

SUBDIVISION OF THE METAMORPHIC TERRAINS

THRACE LITHOTECTONIC UNIT

Biotite gneisses (Tr/bg)

Thrace Unit is represented only by rocks of the pre-Triassic-Jurassic basement, which is strongly fragmented by the block movements in the Zvinitsa ring structure. In the exposed in the structure blocks are distinguished porphyritic, equigranular and aplitoid metagranites plus their frame consisting of biotite gneisses irregularly alternating with amphibolites and the incorporated in them lenses of metagabbro (Yordanov et al., 2008).

STRATIGRAPHY OF THE CENOZOIC

PALEOGENE

Terrigenous group

Conglomerate-sandstone formation (cgsE3)

The formation is built of multiple alternations of rusty yellow equigranular sandstones and subordinate siltstones. In places the sandstones grade into pebbly conglomerates.

The sandstones are the major rock type. In most places they are indistictly bedded. Their structure is massive and their texture is aleuritic to coarse-psammitic. By composition they are polymict, the clastic

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grains corresponding to the composition of the metamorphic basement. The sandstones commonly grade into grey-yellow, fine-grained to silty, strongly calcareous varieties.

Svobodinovo Volcano-Sedimentary Group

Padartsi Formation (PdE3)

The formation is built of predominant thinly rhythmic alternation of sandstones, siltstones, marlstones, calcareous tuffs, and intermediate tuffs. It is distinguished for the presence of distinct horizontal bedding. The sandstones are grey, beige or creamy, commonly with massive structure and medium to thick stratification. The siltstones display similar characteristics. They differ from the sandstones by their grain size and by forming mainly thin- to medium-bedded packages. The marls occur in the form of thin continuous layers. They are grey, light beige to beige, laminated, micro-grained or dense. The tuffs are grey-yellowish or green-greyish psammitic rocks which occur in the form of layers and lenses of variable thickness.

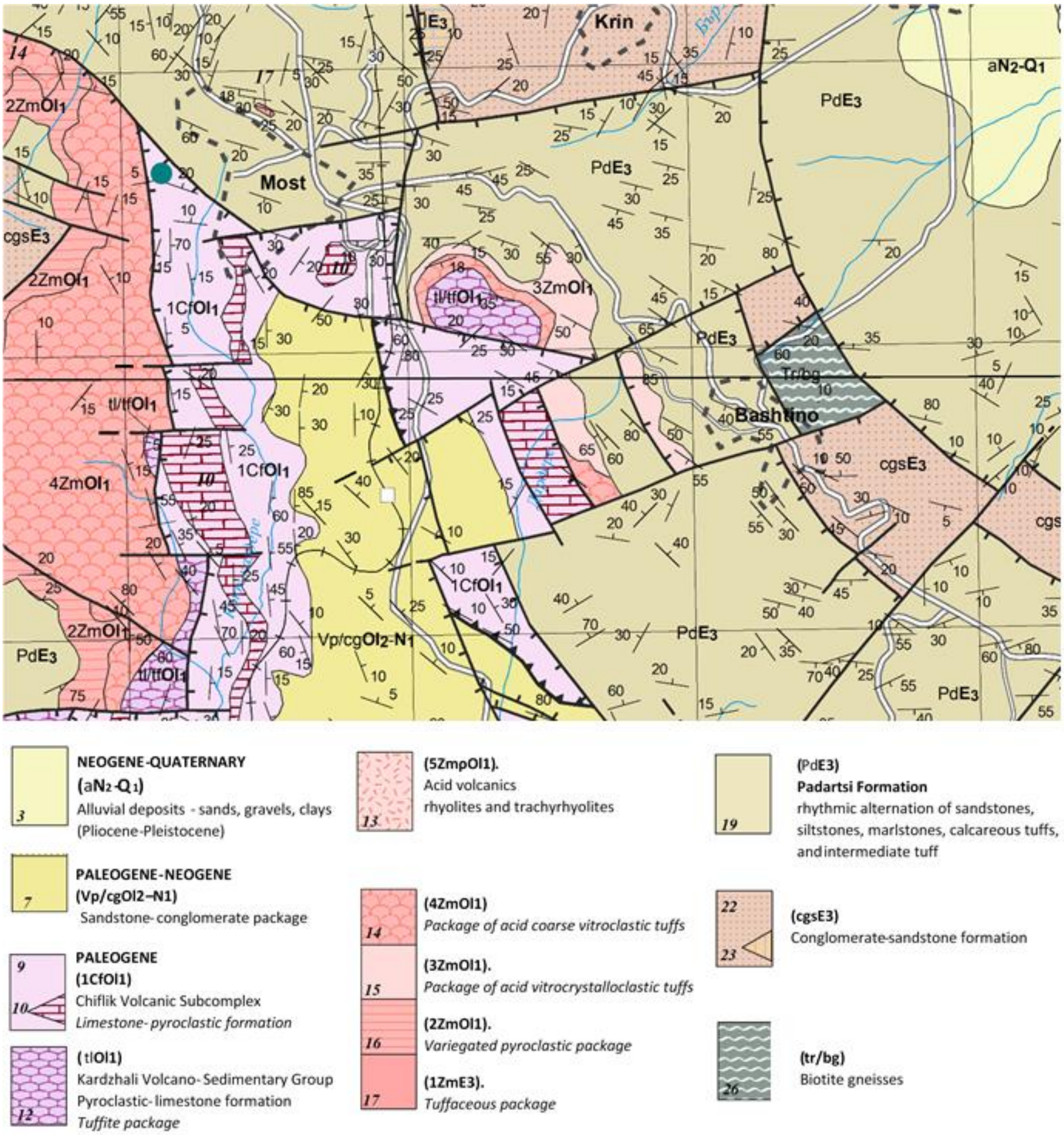

Fig. 2: Geological map of the studied area (on Yordanov, B. et al. Map sheet K-35-76-V (Knizhovnik). Geology and Geophysics JSCo, Sofia, 2008.)

Kardzhali Volcano-Sedimentary Group

Zimovina Volcanic Complex

Tuffaceous package (1ZmE3)

The package is built of relatively thin beds or lenticular discontinuous bodies of acid tuffs interlayered in the upper levels of the section of the Padartsi Formation. The tuffs are white to pale reseda, massive fine ash to ash, with crystalloclasts of biotite and plagioclase, totally altered virtroclasts, and sporadic lithoclasts

Package of acid vitrocrystalloclastic tuffs (3ZmOl1)

The pyroclastics overlie with sharp lithologic boundary sediments of the Padartsi Formation. They are respectively covered in concordant manner by rocks of the other packages of the tuffite-tuffaceous formation.

The unit is built of a shortly changing in vertical and lateral direction sequence composed of various by colour (grey, ochre, reseda and whitish), size, and clast type acid tuffs.

Package of acid vitrocrystalloclastic tuffs (3ZmOl1)

The tuffs overlie concordantly, with sharp lithologic contact sediments of the Padartsi Formation.

The package comprises ash to coarse ash, mainly reseda to whitish pyroclastics with ashfall origin.

Package of acid coarse vitroclastic tuffs (4ZmOl1)

These specific rocks are products of thick pyroclastic flows. The unit overlies concordantly, with sharp lithologic contact, or intertongues with rocks of the package of acid vitrocrystalloclastic tuffs, or normally, with sharp lithologic contact sediments of the Padartsi Formation. It is covered concordantly by rocks of the limestone-pyroclastic formation of the Chiflik Volcanic Subcomplex, or by the tuffite package of the pyroclastic-limestone formation.

Acid volcanics (5ZmpOl1)

The unit is composed mainly of fluidal rhyolites, trachyrhyolites, lavabreccias (vent facies), and perlites.

Pyroclastic-limestone formation (tlOl1)

In the complete volume of this unit are distinguished two packages – lower, predominantly limestone, and upper, predominantly tuffaceous, but only the second one is represented in the area of the map sheet.

Tuffite package (tl/tfOl1)

The package is built of yellow ochre, greyish or creamy, calcareous tuffites and fine ash to ash tuffs, commonly with high carbonate content.

Nanovitsa Volcanic Complex

Chiflik Volcanic Subcomplex

Limestone-pyroclastic formation (1CfOl1)

In the range of the map sheet the formation is composed mainly of varied acid pyroclastics and reef-like limestones. Massive to thick-bedded tuffs and subordinately thin- to medium-bedded ashfall tuffs predominate. Continuous layers and lenses of acid pyroclastics, which are enriched in intermediate accessory lapilli, are observed between them (Yordanov et al., 2008).

PALEOGENE-NEOGENE

Valche pole Formation

Conglomerate package (Vp/cgOl2–N1)

The lithology of the package comprises mainly alternating varied sandstones, conglomerates, calcareous and clayey siltstones, as well as sporadic interlayers of acid tuffs.

Predominant are polymict sandstones with white to yellow-grey color, which are thick-bedded in the lower levels, showing horizontal and cross bedding (Yordanov et al., 2008).

NEOGENE-QUATERNARY

Alluvial deposits (aN2-Q1)

The deposits cover with erosional, uneven contact Neogene and Paleogene sediments plus metagranites. Their upper boundary with the alluvial deposits of Pleistocene age has the same pattern.

At the base the Pliocene-Pleistocene deposits are built of unsorted to poorly sorted, well-rounded polymict gravels (with various clast size) and inequigranular rusty brown sands (Yordanov et al., 2008).

Results

Pale green zeolites are composed mainly of glass volcanic debris, fewer crystalloclasts and least lithoclasts. The glass fragments are prismatic in shape, small oysterite to siltstone in size. Between them are isometric corner fragments, some of which are pumice. The glass is acidic, isotropic. Thin edges of anisotropic clay products from the montmorillonite group are observed around the glass fragments. They are also increased on the walls of pumice stones.

Clinoptilolite has formed in the internal cavities of the glass pieces or in the gaps between several glass fragments at the expense of the glass. It is microcrystalline, almost isotropic. Its crystals are most often oriented from the glass walls to the inside of the gaps (Figure 3a, b, c, d). Debris was found, which was completely changed into clinoptilolite. In them the periphery to the interior has an orientation of the crystals, while in the central parts they are in disarray.

Crystal clasts are plagioclase, potassium feldspar, biotite, amphibole, muscovite and others. They are small to microscopic.

Lithoclasts are rhyolite and other rocks fragments and are in limited quantities.

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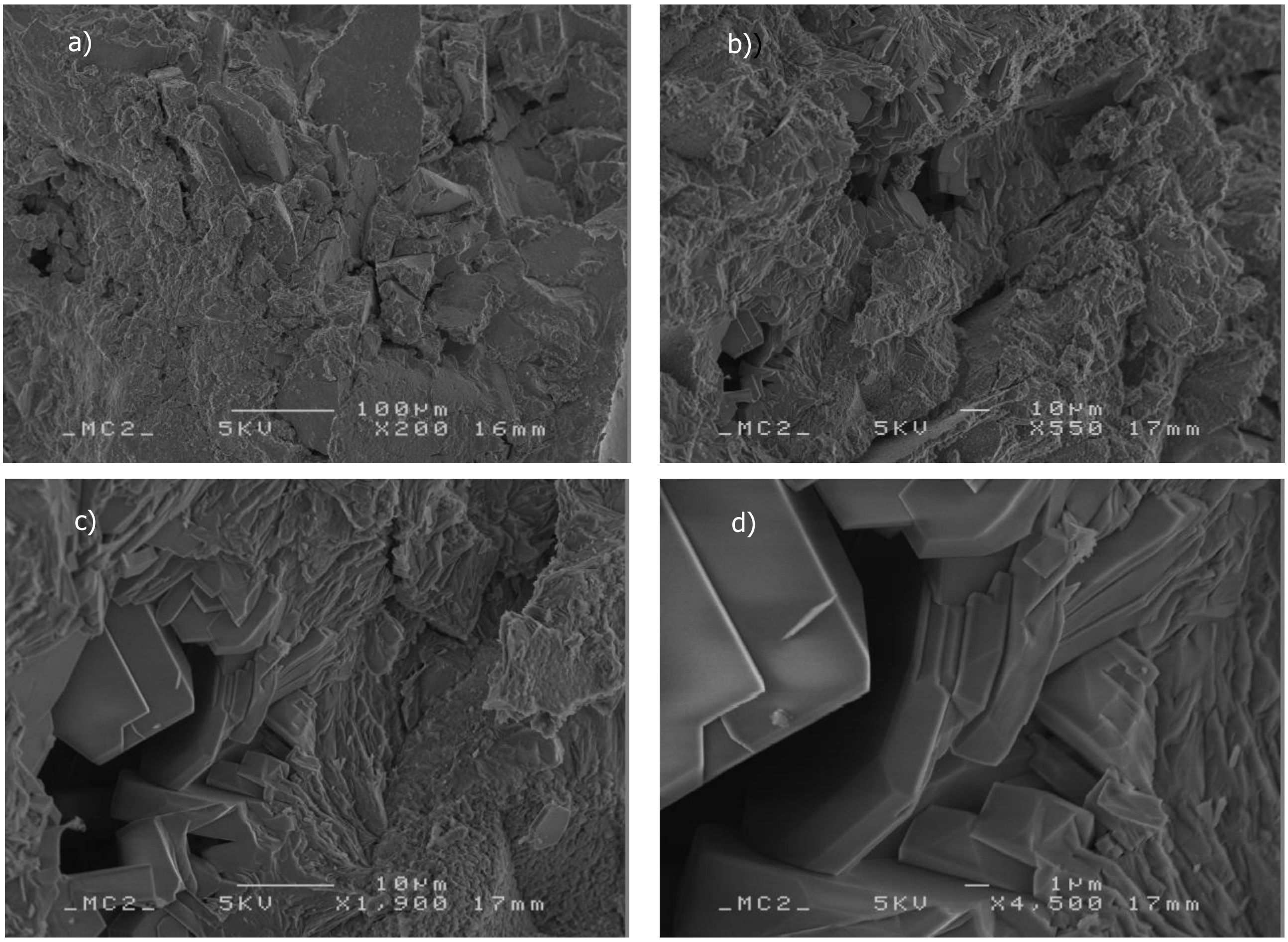

Fig. 3: SEM of (sample №2008 / 1) - "Most" deposit a) glass volcanic fragments SEM x 200; b) SEM x 550 glass volcanic debris; c) clinoptilolite crystals oriented inwards in glass debris cavities, SEM x 1 900; d) clinoptilolite crystals, SEM x 4,500

In reddish-pink clinoptilolite rocks, the clinoptilolite is formed at the expense of volcanic glass, being evolved in the debris and in the gaps between them. It is represented by fine, elongated prisms or tiles, oriented perpendicular to the contact with the glass table. Cord-like formations of anisotropic clay minerals from the montmorillonite group, which have a creamy-yellowish color, are observed almost everywhere in the boundary between the fragments. Crystal clasts are represented by plagioclase, potassium feldspar, pyroxene, quartz, biotite, etc., and lithoclasts by volcanic rocks.

In some places, in the pink-reddish clinoptilolite zeolites West of the village of Most, the presence of manganese oxides and hydroxides, forming thin crusts up to 4-5 mm thick, deposits and impregnations with black color was carried out. Data from diffractometric X-ray analyse shown that they are mainly cryptomelane ($KMn8O6 + H2O$).

Cryptomelane is yellowish-white with a fine-fiber structure, anisotropic, under a microscope, in reflected light. In the central part of completely changed, zeolitized pieces of volcanic glass its also found as well as in the gaps between them (Figure 4a, b). Cryptomelane is often deposited in the central part of cavities lined with transversely grown, elongated prismatic or plate clinoptilolite individuals. In places, cryptomelane fills oval or elliptical cavities in clinoptilolite zeolites (Figure 4c, d).

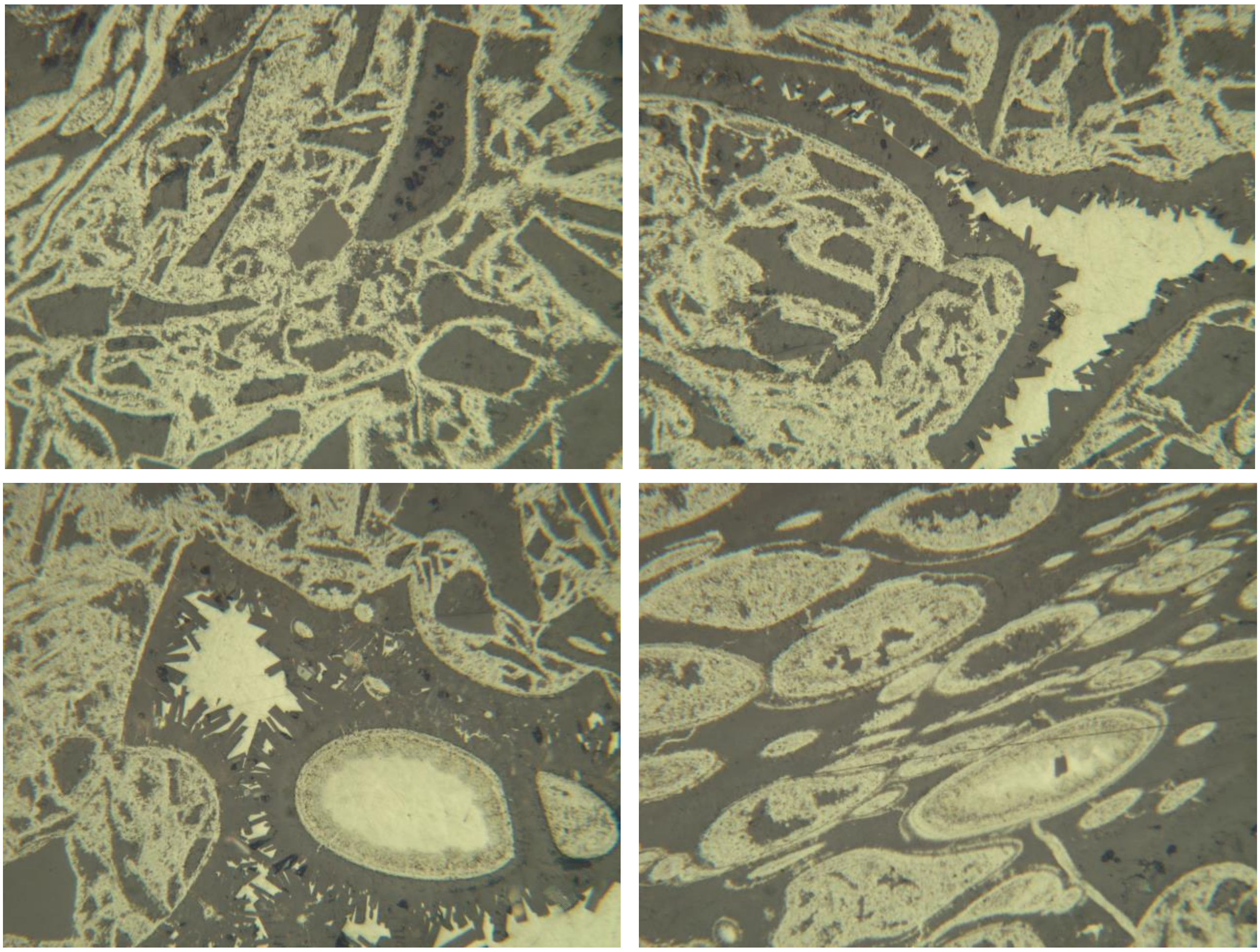

Fig. 4: Sample №2008/4. Cryptomelane in clinoptilolite zeolites from the Most deposit; (a) cryptomelane (yellowish white) deposited in gaps between zeolitised glass particles (dark gray); b, c) cryptomelane (yellowish-white) deposited in the central part of cavities lined with transversely growing elongated prismatic clinoptilolite individuals (dark gray); d) cryptomelane (yellowish white) filling elliptical voids in clinoptilolite zeolites. Reflected light without analyzer. Visible field length 0.53 mm

Discussion

In the current research for the Most deposit, the presence of manganese oxide mineralization was established for the first time.

Manganese mineralization is represented mainly by cryptomelane and todorokite, which are microporous minerals, referred to octahedral molecular sieves (OMS) and octahedral layered materials (OL). They are considered as modern, extremely promising materials with possible applications such as molecular and ionic sieves, sorbents of heavy metals (Pb, Cd, As, etc.) and radionuclides. Unlike of the zeolites, which are aluminosilicate tetrahedral molecular sieves with a pore size of about 3.5 Ǻ, manganese hydroxides are octahedral molecular sieves, which are characterized by a larger pore size, respectively for OMS - 2 (cryptomelane) - 4.6Ǻ and for OMS -1 (todorokite) - 6.9Ǻ.

A case study of a potential repository for highly active radioactive waste is that in the Yucca Mountains, Nevada, due to the cation-exchange capacity of natural zeolites, clinoptilolite and mordenite. In fact, the presence of zeolites in the Yucca Mountains and the cationic exchange of minerals first drew attention to volcanic tuffs as possible repositories for radioactive waste (Bish, 1999). Studies of natural zeolites in the Yucca Mountains of the United States over the past thirty years illustrate that many different aspects of zeolite mineralogy are fundamentally important in the isolation of radioactive waste (Bish et al., 2003). It is interesting from this point of view to study the sorption of heavy metals and radionuclides from natural zeolites, such as those available in Bulgaria

Conclusion

The natural zeolite raw material containing cryptomelane and/or todorokite combines different types

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of microporous minerals and is of great interest in order to clarify its application possibilities to solve a number of problems - purification of heavy metals contaminated mine and industrial waters, soil reclamation, insulation materials and coverage in radioactive waste repositories.

Unlike of the zeolites, which are sorbents for short-lived radionuclides, manganese hydroxides are selective sorbents for long-lived radionuclides and are important as a component of the geological environment that may potentially store high-level radioactive waste.

The importance of zeolites in our research of the region in ecological aspect extends far beyond the simple cation-exchange interactions to the applications for solving the problems of storage and isolation of radioactive waste. The present work provides a basis for further research on volcanic tuffs in the area as a possible repository for radioactive waste.

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