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Physical-Chemical and Mineralogical-Petrographic Examinations of Trepel from Republic of Macedonia

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Abstract:-*In this paper are shown results of the physical-chemical and mineralogical-petrographic examinations of trepel from Brod-Gneotino, Bitola region, Republic of Macedonia. According to the scanning electronic microscopy (SEM), the infra-red (IR) and powder X-ray (XRPD) examinations, it was determined that examined trepel is composed mainly of opal (of biogenetic origin) as well as quartz, illite – hydromicas, feldspars (plagioclases, feldspars), and chlorites of minor importance. DTA and TGA examinations show results which are in line with the determined mineralogical composition of the sample. With these examinations it is concluded presence of organic matter in the sample. As result of these examinations it can be concluded that this raw material (trepel, natural mixture of diatomite and clay minerals) can be used as raw material for production of ceramic products (based on classical and hydrothermal technology), for synthesis of zeolites, as absorbent for cleaning of raw industrial waters.*

Keywords:- *Trepel, opal, diatomite, SEM, IR, XRPD*

1. INTRODUCTION

Trepel is a natural mixture of diatomite and clay minerals. Recent excavations of the coal deposits from the area of the Brod-Gneotino (Bitola region), are forced to mining works as result of a thick wall trepel layer, the thickness of which is several meters (cca 50–70 m). Physical-chemical and mineralogical-petrographic examinations show that this non-metal raw material can be used as basic component for production of light insulating construction materials, production of thermal insulators, production of lightweight construction materials, for the synthesis of zeolites, purification of industrial waters, in the cement industry (as pozzolanic material), as pesticide holder, as well as for improving the physical and chemical characteristics of certain soils.

2. EXPERIMENTAL SECTION

During this research following examinations were performed: macroscopic examinations, chemical examinations, XRD examination, DTA/TGA examinations, microscopic examinations (light microscopy and SEM).

Macroscopic Examinations

Examined trepel sample from Brod-Gneotino (Bitola region) represents a sedimentary rock (of biogenetic origin) with grayish to grayish-white color, very light and soft (1–2 by Mohs), fine to superfine grained structure, porous, shell-like break, tongue sticky etc. (Fig. 1).

Fig 1: *Sample of trepel from Brod-Gneotino (Bitola region), Republic of Macedonia*

The physical properties of the examined trepel are shown in table 1.

Table1: *Physical properties of trepel*

Property	*Value*
Bulk density	0.77 – 0.93 g/cm^3
Water absorption	67 – 79 %
Open porosity	52-67 %
Total porosity	67-76%
Specific mass	2.45 g/cm^3

Chemical Examinations

The chemical examination of trepel was performed with the classical chemical silicate procedure. The results of this examination are shown in table 2.

Table 2: *Results of chemical examinations of trepel*

Oxide	*Mass (%)*
SiO_2	55.86
Al_2O_3	15.29
Fe_2O_3	8.28
CaO	2.90
MgO	2.78
K_2O	2.00
Na_2O	2.33
SO_3	0.69
LOI	9.60
Total	99.77

Mineralogical Examinations

The mineralogical examinations of trepel are performed with XRD powder diffraction and microscopy.

XRD Examinations

The XRD powder analysis was performed on the DRON X-ray diffractometer (Cu Kα radiation, Wavelength λ=1,54056 mm, Testing interval - 70°, Registration voltage 38 kV, Current intensity 18 mA). Results of the examination of trepel are shown in Fig. 2.

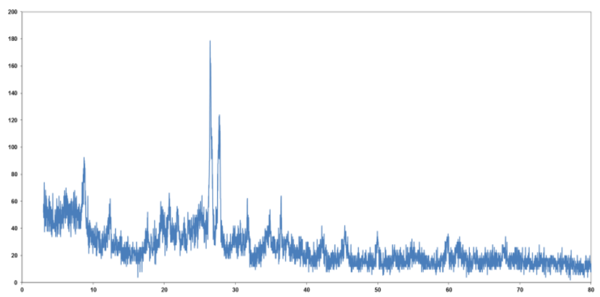

Fig 2: *X-ray spectra of trepel from Brod-Gneotino (Bitola region), Republic of Macedonia*

With the XRD examination of trepel the following minerals are identified:

- quartz,
- feldspars,
- chlorites,
- illite-hydromica

Trepel contains amorphous silica which causes the bulge in the background peak levels.

Microscopic Examinations

Microscopic examinations of trepel included: light microscopy and scanning electron microscopy.

Light Microscopic Examinations

The microscopic examinations (performed with the polarizing translucent light) show that the sample is characterized with a micro-cryptocrystalline ground mass of optic isotropic nature. This groundmass of trepel is composed of opal inside of which there are very fine to super fine grained quartz, feldspars, chlorites, illite-hydromica.

Opal products with irregular fibrous forms remembering of roots of vegetative origin can be also rarely encountered in the thin section.

The globular structures (of vegetative origin) of opal are quantitatively predominant in the examined trepel sample. The rock structure is globular –isotropic, while the texture is massive – homogenous.

Scanning Electron Microscopy Examinations

The SEM examinations confirm the microscopic polarizing results especially from point of view that the globular structures have biogenetic nature. Completed and fragmented globules of alga Diatomeae are shown on the SEM-pictures where disks resembling to disks of sunflower with or without peripheral ends. It's evident that the globules of vegetative origin belong to two or more different types. These "sunflower" disks are completely perforated with discrete caverns, hollows along the total disk surface. It's evident also that the trepel porosity is connected with the abovementioned caverns inside the surface of the globular structures (Fig 3, 4).

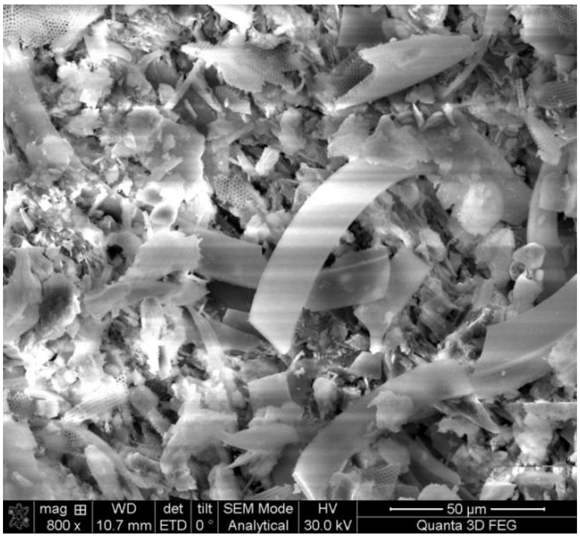

Fig-3: *SEM-photo of a common trepel mass composed of numerous microrelics – opal globules of biogenetic origin*

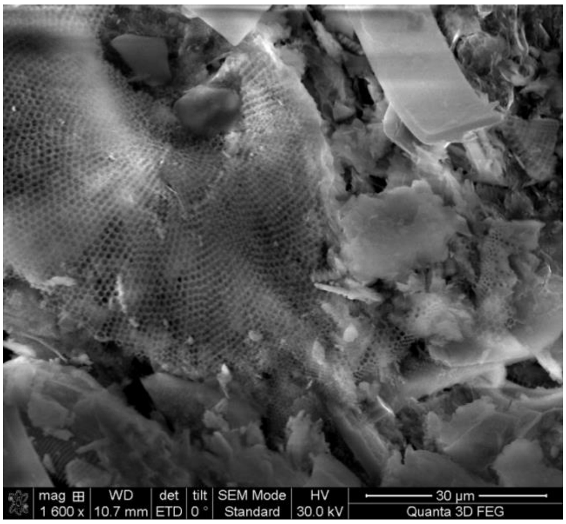

Fig 4: *Sample of trepel(microfossil - diatomite)*

Thermal Examinations

DTA/TGA analyses of the trepel were performed with Stanton Redcroft, England – apparatus, under the following experimental conditions: Temperature range - 20 – 1000 °C; speed of heating 10 °C/min; sample mass 13.57 mg; gas environment – air; material carrier – ceramic pot. Results of the differential-thermal analysis and the thermo-gravimetrical analysis of the trepel are shown in Fig.5.

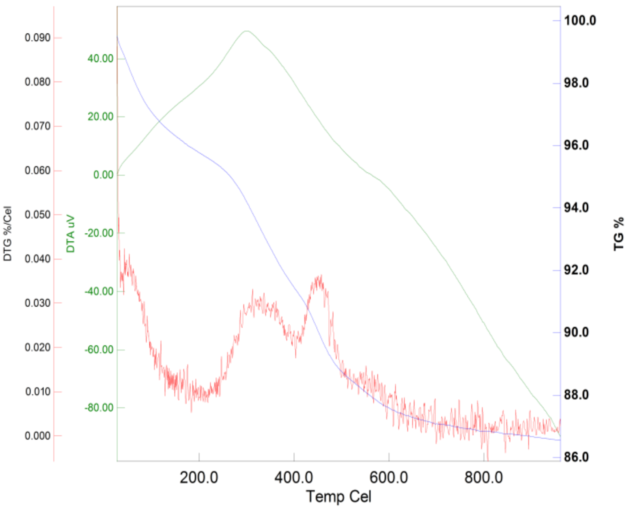

Fig -5: DTA/TGA examinations of trepel

Based on the DTA/TGA examinations showed on Fig. 5 the following can be concluded:

- The DTA curve shows a wide endothermic peak with a minimal value of 180 °C which is as result of separation of the rough water bonded to the clay minerals and opal component. At the same curve evident is the presence of two exothermic peaks with maximum values of 323 °C and 454 °C which are as result of burning of organic matter in trepel.
- Based on the TGA curve it can be concluded that during the heating process evident is the loss in mass. At the temperature interval 108 °C and 260 °C there is a mass loss as result of separation of bonded water from the opal component and the clay minerals. In the temperature interval 260 °C – 500 °C is the most intensive loss in mass as result of burning of the organic component. In the temperature interval over 500 °C the thermo-gravimetric curve continues to show loss in mass, though this loss is with much lower intensity. In this interval there is dehydration of the clay component and the opal component [1-3].

IR Examinations

Infra-red spectroscopic examinations of trepel are shown in Fig 6.

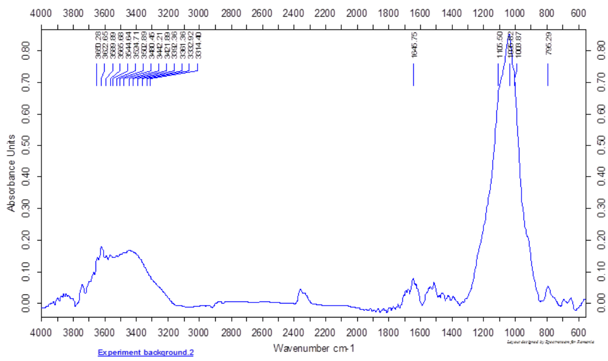

Fig 6: *IR spectra of trepel from Brod-Gneotino*

IR spectroscopy is a widely used method when examining amorphous SiO_2, and especially when studying the way the hydroxyl groups are bonded on the surface of the amorphous SiO_2.

The absorption bands at 1645, 1105 and 795 cm^{-1} are as result of the presence of the amorphous SiO_2 in trepel. The main Si-O band for amorphous SiO_2 is at 1036 cm^{-1}, which in this case is shifted towards the smaller values of the frequency which is as result of the substitution of the Si^{+4} ions in the tetrahedral position with trivalent cations.

Absorption bands at 550 cm^{-1}, 630 cm^{-1}, 720 $cm^{-1}$and 1003 cm^{-1} are as result of the presence of feldspar in trepel.

The absorption band at 3442 cm^{-1} is as result of the presence of hydroxyl groups in trepel as well as result of the presence of absorbed H_2O. The absorption band at 3622 cm^{-1} is another evidence of the presence of the absorbed H_2O, while the band at 1650 cm^{-1} is due to the presence of hydroxyl groups.

3. CONCLUSIONS

Based on the examinations performed on trepel (as a natural mixture of diatomite and clay minerals), a material obtained from the area of Brod-Gneotino (Bitola region), Republic of Macedonia, the following is concluded:

- The bulk density of treper is determined to be 0.77 to 0.93 g/cm^3, while the water absorption is between 67.38 to 79.32%. According to these values of bulk density and water absorption the open porosity of the samples is between 52.27 and 67.66%.
- The examinations show that trepel is a non-metallic raw material that contains 55.86 % SiO_2.
- Roentgen-structural examinations show that the probe contains the following minerals: opal (of biogenetic origin), quartz, illite – hydromicas, feldspars (plagioclases, feldspars), and chlorites. Whereas the wide peak shows presence of the amorphous matter in the sample.
- DTA/TGA examinations show results which are in line with the mineralogical composition of the material. With these examinations it is concluded the presence of organic matter in the sample.
- IR spectroscopic examinations confirm the XRD examinations as well as DTA/TGA. IR confirms the presence of amorphous SiO_2 in trepel, as well as presence of feldspar. At the same time, the IR examinations show presence of absorbed H_2O, strongly H-bonded hydroxyl groups and OH-hydroxyl groups.

As result of these examinations, it is concluded that trepel can find application in the industry of construction materials [4-7].

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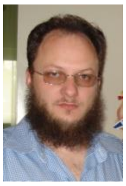

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Dr. Blagoj Pavlovski *PhD* - full professor, Inorganic Technology currently in pension, graduated in 1967 in the Faculty of Technology and Metallurgy in Skopje, while in the period 1973-1976 in Aachen, Germany got his PhD. Dr. Pavlovski has published over 120 professional and scientific publications (some papers published in the United States of America, Germany, Netherlands, Italy, and Hungary etc.) in the field of non-metals and it's a holder of 5 patents. Dr. Pavlovski during his career was in the various functions. He served as the Head of the Institute for Inorganic Technology at the Faculty of Technology and Metallurgy, President of the Faculty Union, President of the Executive Board of Union for education in the chemical industry, President of the Section for Nonmetals in the Union of Chemists and Technologists of Macedonia, Vice Dean and then Dean at the Faculty Technology and Metallurgy – University St. Cyril and Methodius. Dr. Pavlovski has greatly cooperated with the industry where he has completed 96 projects, whilst with the ministry of Science and Educations has completed 6 projects.

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