Research Article

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Effect Of Thermal Treatment Of Trepel At Temperature Range 800-1200˚C

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Abstract: Trepel is the local name for a mixture of diatomaceous earth and clay minerals. It represents a greyish, soft, very light, weakly cemented, fine biogenetic sedimentary rock. The studied material is taken from the vicinity of Bitola city (Republic of Macedonia). Here, trepel was treated up to three temperature intervals (800, 1000 and 1200ºC) for a period of 1 hour. The X-ray powder diffraction results indicate the presence of both an amorphous phase and the following crystalline phases: quartz, feldspars (plagioclase), mica (muscovite) and chlorites. The results of SEM analysis revealed skeletons of alga Diatomeae with nano-pores. By thermal treatment of the samples, a gradual change in color as well as higher bulk density and compressive strength was observed. The increase of the temperature, in addition, affected the mineralogical composition and increased the presence of the amorphous phase (aluminasilicate glassy phase). SEM results of the thermally investigated samples depicted morphological changes expressed by shrinkage of the pore diameters in comparison to the initial material. The major and minor constituents were established by chemical analysis revealing the following chemical composition of raw trepel: SiO_2 (63.65 wt%), Al_2O_3 (11.76 wt%), Fe_2O_3 (5.93 wt%), MnO (0.13 wt%), TiO_2 (0.63 wt%), CaO (1.42 wt%), MgO (2.22 wt%), P_2O_5 (0.11 wt%), K_2O (1.63 wt%), Na_2O (0.92 wt%), LOI (11.50 wt%).

Keywords: Trepel; diatomaceous earth; clay minerals; characterization; thermal treatment.

1 Introduction

Republic of Macedonia is rich in inorganic materials with a wide spectrum of potential use and application [1-4]. Trepel, found in the vicinity of the Bitola power plant, takes a special place amongst non-metallic materials because it represents a mixture of diatomite and clay minerals [5-14]. It represents a biogenetic rock; grayish, soft, very light, weakly cemented, finely opal sedimentary rock [9]. The results from the physical-chemical and mineralogical-petrographic characterization show that this non-metallic raw material can be used as the basic component in the production of light insulating construction materials, thermal insulators, lightweight construction materials, for the synthesis of zeolites [15], purification of industrial waters [16], in the cement industry (as pozzolanic material) [17-24] as pesticide holder, as well as for improving the physical and chemical characteristics of certain soils.

According to the physical-chemical and mechanical properties, trepel is similar to diatomite relying to the compressive strength in natural state, porosity, water absorption, and specific density. Trepel contains clay minerals (muscovite, chlorites and plagioclase) and its diverse chemical composition makes it an appropriate substance for the production of porous construction and adsorbent material.

The economic effect of using trepel is based on its fine microstructure and presence of amorphous phase. These properties makes the material highly reactive and utilized as raw product, instead of its treatment as a waste. Therefore, it is used for the production of ceramics at relatively lower temperatures compared to

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the classical ceramic raw materials (quartz, feldspars and clay minerals). In addition starting at 1000°C, a mullite is formed as by-product which does not occur when other classical ceramic raw materials are utilized, adding high mechanical properties (compressive strength) of the obtained products.

During the usage of trepel as a basic material in the industry for production of ceramic materials, of great importance are the mineralogical changes that occur within trepel during the thermal treatment (i.e. during the sintering process). Due to this fact, the subject of this research paper is the effect of the thermal treatment of trepel in the temperature interval from 800-1200°C.

2 Materials And Methods

The raw material (locally known as trepel), was taken from the Bitola region, Republic of Macedonia.

The chemical composition of raw trepel was determined with the classical silicate analysis. Crude trepel was melted in a mixture of carbonates, whereas the percentages of various oxides present in the material are determined with complexometric titration. The alkali metal oxides (Na_2O and K_2O) were determined with a flame photometry. The determination of the trace elements was performed with Inductively Coupled Plasma Mass Spectrometry (ICP-MS, Agilent 7500cx).

For the purpose of the thermal investigations, raw trepel was first crushed and ball-milled for a period of 2.5 h. After a powdering procedure of trepel, 5% of distilled water was added. Then, the mixture was placed in a hermetically closed desiccator for 24 h to achieve the distribution of an even moisture level throughout the mixture. The samples were prepared as cylindrical forms with a diameter of 20 mm and an height of 10 mm under pressure from 2 MPa. Samples were sintered at three temperatures: 800, 1000 and 1200°C for a period of 60 min. The sintered trepel samples were subjected to compression testing by using an hydraulic press (Automax 5 – Controls). A minimum of three samples were tested under the same conditions. Upon testing, the material was characterized by physico-mechanical methods. The mineralogical composition was further analysed by XRPD. For each temperature interval, three samples were tested.

The mineralogical characterization of trepel was carried out by an X-ray powder diffraction (XRPD), thermal analysis (TGA/DTA), scanning electron microscopy (SEM-EDX), transmission electron microscopy (TEM) and infrared spectroscopy (IR).

XRPD analysis was performed on Rigaku Ultima IV X-ray diffractometer equipped with D/teX high-speed 1-dimenzional detector using Cu$K\alpha$ radiation (λ = 1.54178 Å) in 2θ range from 5 to 60°. The accelerating voltage and the current power were set to 40 kV and 40 mA, respectively.

DTA/TGA analyses of trepel were performed in an air environment with Stanton Redcroft apparatus, under the following experimental conditions: temperature range from 20–1200°C; speed of heating set to 10°C/min; sample mass of 13.577 mg, using ceramic pot as a material carrier.

Scanning electron microscopy VEGA3 LMU coupled with energy dispersive X-ray spectroscopy (INCA Energy 250 Microanalysis System) was used to quantitative analyze the material. The accelerating voltage of the SE detector was set to 20 kV.

The Perkin-Elmer FTIR system 2000 interferometer was engaged to record the IR spectra in 4000–500 cm^{-1} range using the KBr pellet method. The pellets were prepared by pressing a mixture of the sample and of dried KBr (sample: KBr approximately 1:200), at 10 tons cm^{-2}.

Ethical approval: The conducted research is not related to either human or animal use.

3 Results And Discussion

3.1 Physical-mechanical properties of trepel

From the physical-mechanical point of view, the examined trepel subject of this research represents a sedimentary rock (of biogenetic origin) with grayish to grayish-white color, soft (1-2 by Mohs) and very light, with fine to superfine grained structure, porous, shell-like etc. The bulk density of trepel is 0.60 – 0.68 g/cm^3, the density is 2.41 g/cm^3, while the compressive strength in natural state (raw) is 3.45 MPa. The physical-mechanical characteristics of trepel are shown below (Table 1 and Figure 1).

3.2 Chemical analysis of raw trepel

The chemical composition of trepel (shown on Table 2) is determined with the classical chemical silicate analysis. Crude trepel was melted in a mixture of carbonates, whereas the percentages of various oxides present in the material were determined with complexometric titration. The alkali metal oxides (Na_2O and K_2O) were determined with a flame photometry. The determination of the trace

Figure 1: Natural (crude) trepel from Bitola region.

Table 1: Physical mechanical properties of raw trepel.

Bulk density (g/cm³)	0.60–0.68
Water absorption (%)	75–81 %
Open porosity (%)	50–60 %
Total porosity (%)	67–71%
Density (g/cm³)	2.41 g/cm³
Compressive strength	3.45 MPa

Table 2: Chemical composition of trepel.

Oxides	Mass %
SiO_2	63.65
Al_2O_3	11.76
Fe_2O_3	5.93
MnO	0.13
TiO_2	0.63
CaO	1.49
MgO	2.22
P_2O_5	0.11
K_2O	1.63
Na_2O	0.92
LOI	11.50
Total	99.99

elements was performed with ICP-MS. The loss of ignition (LOI), is determined while heating raw trepel at 1000 °C for a period of 1 hour was 11.5%. The results obtained from the chemical composition of trepel indicate that the analyzed material represents an acidic rock with prevailing percentage of SiO_2 (63.65%) and substantial content of Al_2O_3 and Fe_2O_3 (11.76% and 5.93). In table 2 and

Table 3: Trace elements determined in the naturally occurring trepel.

Trace element	Content/ppm
Cu	113
Cr	111.2
Ni	40.7
Co	22.7
Zn	3.59
V	112.8
Pb	10.3
Cd	0.060
As	5.9
Se	3.2
Tl	0.97
Bi	0.57
Ba	459.6
Rb	114.2
Sr	166.6
Cs	4.2
Th	9.6
U	7.7
Mo	1.6
Sn	2.8
Sb	0.2
Pd	0.6
Ag	2.5
Ga	16.6
Ge	1.0
Li	32.73
Be	2.6
B	<10

table 3 is shown the chemical composition of oxides and trace elements.

3.3 X-ray powder diffraction analysis of raw trepel

XRPD pattern of trepel (Figure 2) mainly depicts crystalline behavior with a small presence of amorphous matter. The crystalline phases are mainly represented by silica (quartz peaks at 20.89°, 26.67°, 39.50°, 50.15°, 59.59°), feldspars

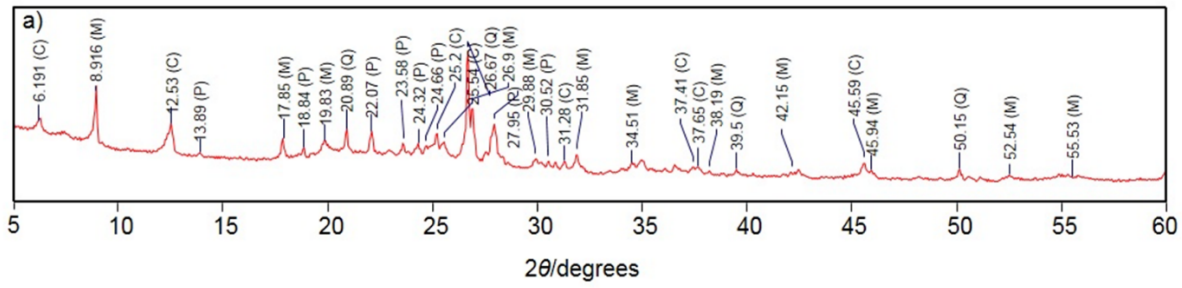

Figure 2: XRPD analysis of raw trepel (Q: quartz, M: muscovite, C: chlorite, P: plagioclase).

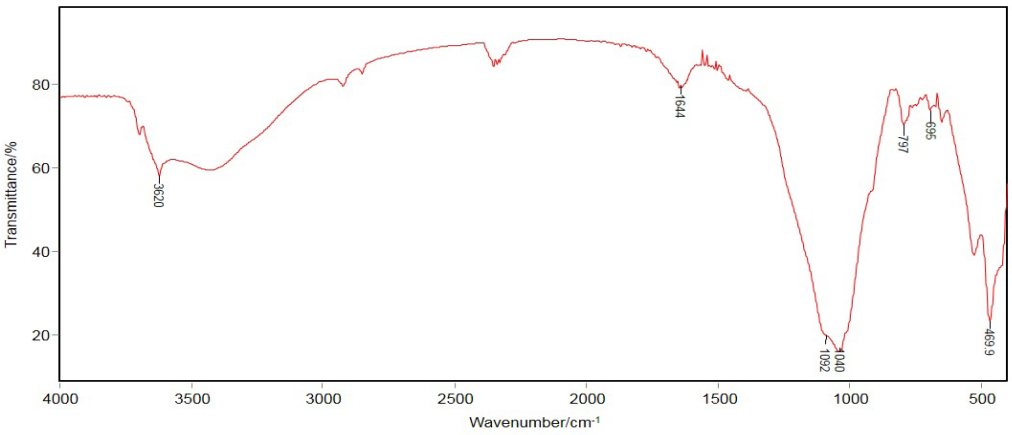

Figure 3: IR spectrum of raw trepel.

(plagioclase peaks at 13.89°, 18.84°, 23.58°, 24.32°, 24.66°, 27.82°, 27.95°, 30.24°, 30.52°), mica (muscovite maxima at 8.91°, 17.85°, 19.76°, 26.90°, 29.89°, 31.85°, 34.51°, 38.19°, 42.15°, 45.59°, 45.94°, 52.54°, 55.53°) and chlorites (peaks at 6.26°, 12.53°, 18.84°, 25.20°, 25.53°, 27.82°, 31.28°, 37.41°, 37.65°, 39.50°, 45.59°, 45.94°).

3.4 Infrared spectral analysis of raw trepel

The IR spectrum of raw trepel (Figure 3) exhibits an absorption band at 797 cm^{-1} attributed to the bending vibrations of Si-O-Si framework, whereas the band at 1061 cm^{-1} is a result of the stretching vibrations of Si-O-Al units. The band at 1644 cm^{-1} is due to bending vibrations from the absorbed water, whereas the band at 3625 cm^{-1} is due to the stretching vibration of the absorbed water molecules [2]. The bands at 469.9 cm^{-1}, 529 cm^{-1} and 695 cm^{-1} are due to the presence of feldspars in the sample. The bands at 797 cm^{-1} and 1080 cm^{-1} are due to the presence of quartz [25-26].

3.5 Scanning electron microscopy (SEM) of raw trepel

The results from the SEM of raw trepel are shown in Figures 4 and 5. The SEM images provide sufficient evidence of the biogenetic nature of the raw material. Various fragments and/or complete skeletal forms of diatoms algae (either in the form of sunflower disks or extended tubes) contain disk or oblong shapes and range from 15 to 60 μm. The observed variations in the shape most likely occur from the clay component in the raw material. SEM morphology of trepel does not indicate preserved form of the diatom frustules.

The EDX spectrum enabled to quantitatively determine the chemical composition. The element weight percentage (C: 4.69%, O: 40.48%, F: 0.77%, Na: 0.69%, Mg: 1.17%, Al: 7.09%, Si: 34.41%, K: 2.30%, Ca: 1.38%, Ti: 0.63%, Fe: 6.38%) confirmed the mixture of diatomaceous earth with the clay minerals.

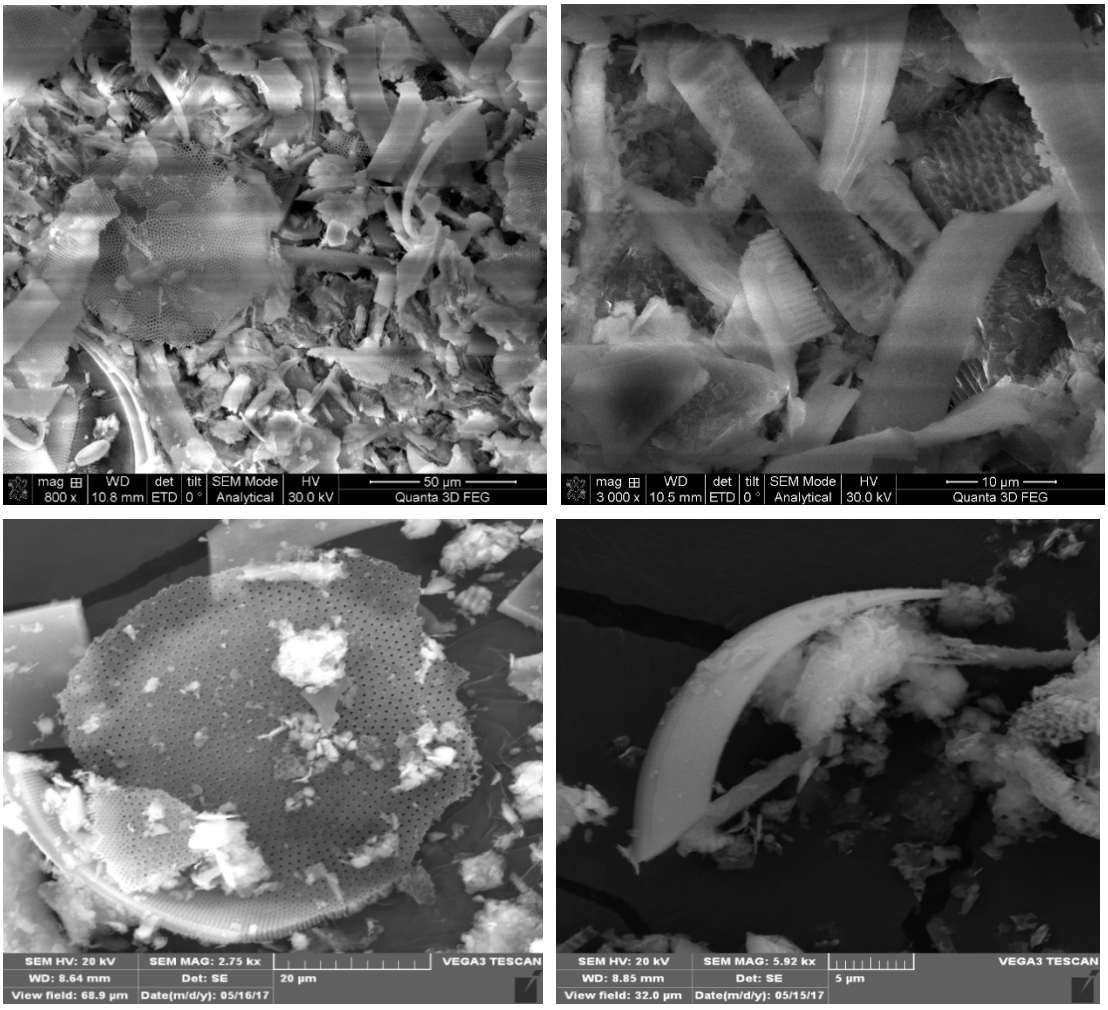

Figure 4: SEM pictures of raw trepel composed of various microrelics of biogenetic origin with various forms (globular or tubes) with many pores ranging from 350 – 650 nm.

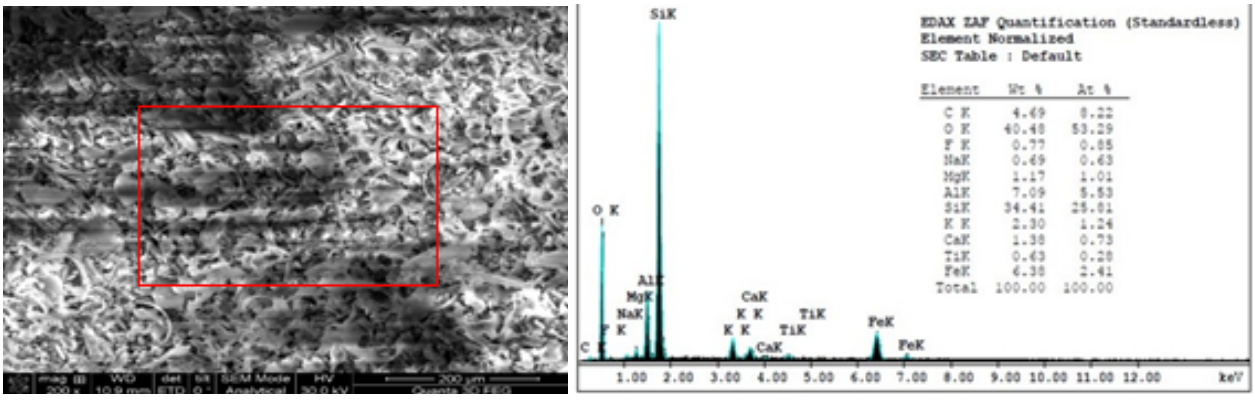

Figure 5: SEM-EDX spectrum of raw trepel.

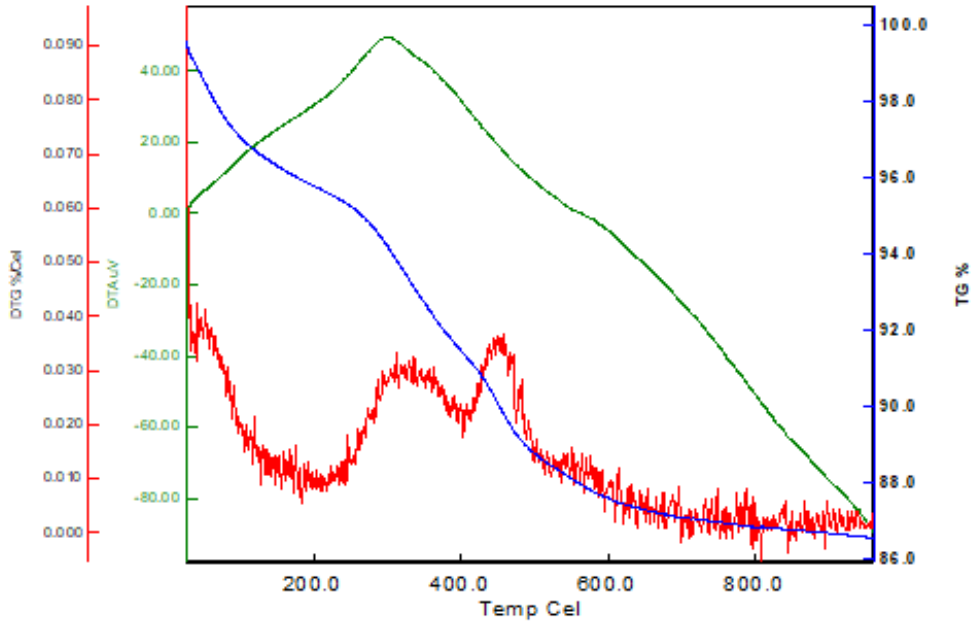

Figure 6: DTA/TGA of raw trepel.

3.6 Thermal examinations of raw trepel

The thermogravimetric analysis (TGA) and the differential thermal analysis (DTA) of the analyzed sample of trepel is shown in Figure 6. The DTA curve shows a wide endothermic peak with a minimal value of 180°C. This peak is a result of separation of the rough water bonded with 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 result of the burning of organic matter present in trepel.

Based on the TGA curve, it is evidence of mass loss during the heating process. The thermogravimetric analysis (TGA) of the analysed trepel indicates weight loss in three temperature intervals (Figure 6). The first temperature interval ranges between room temperature and 100°C resulting in 2.9% mass loss, attributed to the free water present in the sample. The second temperature interval occurs between 108°C and 600°C with mass loss of 9.55%. This temperature interval is attributed to dehydroxylation of the clay component (muscovite and chlorite) as well as the burning of the present organic matter present in the raw material. The third temperature interval occurs at temperatures higher than 600°C. There, thermogravimetric curves continually show lower intensity of mass loss (1%) ascribed to the dehydration process of the opal component.

3.7 X-ray powder diffraction analysis of thermally treated trepel samples

Results of the XRPD analysis of the thermally-induced trepel at 800°C, 1000°C and 1200°C (Figure 7b–2d) demonstrated crystalline behavior with a small amount of amorphous phase. The crystalline phase is represented mainly by quartz, muscovite, feldspars and chlorites. However, the increase of the temperature expanded the amount of the amorphous phase in the sample. The appearance of the complex positioned "bump" between 15 and 28° (2θ) is attributed to the transformation of the crystalline mass into aluminosilicate glass. During the thermal treatment of trepel, a slight decrease of the quartz phase was monitored (at 1200°C), but formation of two new phases was evidenced – mullite (maxima at 16.33°, 25.86°, 26.19°, 33.29°, 35.07°, 40.65°, 40.98°, 42.40°, 54.33°) and tridymite (maxima at 20.80°, 21.63°, 24.23°, 32.65°, 35.71°, 44.30°).

3.8 Shrinkage of the samples after compressing and heat treatment

Physico-mechanical features of the thermally treated samples (Figure 8) indicate gradual change in colour from ochre to black as the temperature increases, accompanied by a gradual increase of the bulk density and abrupt rise of

Table 4: Physical-mechanical properties of cylinders of raw trepel compared to the sintered samples at 800, 1000 and 1200°C for a period of 60 min.

Temperature (°C)	Bulk density (g/cm³)	Compressive strength (MPa)	Mass (g)	Diameter (mm)	Shrinkage (%)
800	0.81	4.40	2.25	19.84	0.80
1000	0.94	14.94	2.17	19.25	3.75
1200	1.30	32.48	2.11	18.26	8.70

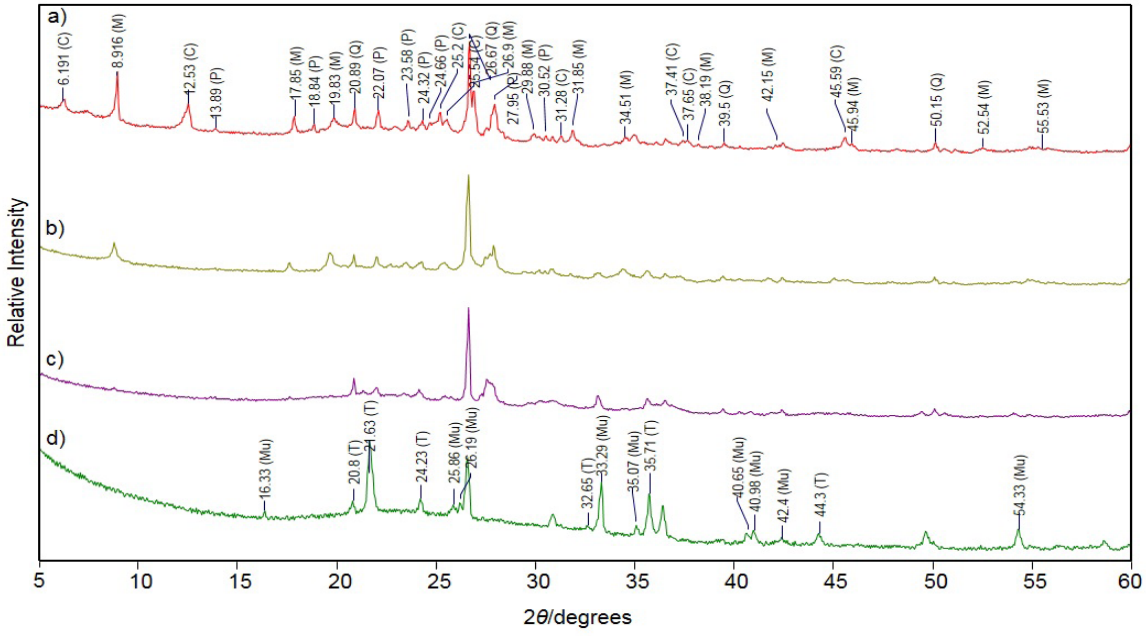

Figure 7: XRPD analysis of raw trepel (a), and thermally treated sample for a period of 1 hour at 800°C for a period of 1 hour, (b) at 1000°C for a period of 1 hour, (c) and at 1200°C for a period of 1 hour (d).

Figure 8: Shrinkage and the obvious change in color of cylinders of trepel sintered at 800, 1000 and 1200°C for a period of 60 min.

the compressive strength (Table 4). In addition, a diameter of the pellets as well as the mass of the samples decreased with ramping the temperature to 800, 1000 and 1200°C. The shrinkage of the diameter ranges from 0.8% at 800°C to 8.7% at 1200°C

The thermal treatment of the samples shows evidence of mineralogical composition changes and amorphous fraction increase.

3.9 SEM of thermally treated trepel

The SEM results of the SE micrographs of the thermally treated samples provided important knowledge (Figure 9) in regards to the morphological changes occurring during the sintering process. Namely, the pores of the various skeletal forms were reduced from the 350– 650 nm to 150–250 nm that is particularly important that can be exploited for the further use and application of the raw material as a filtration source.

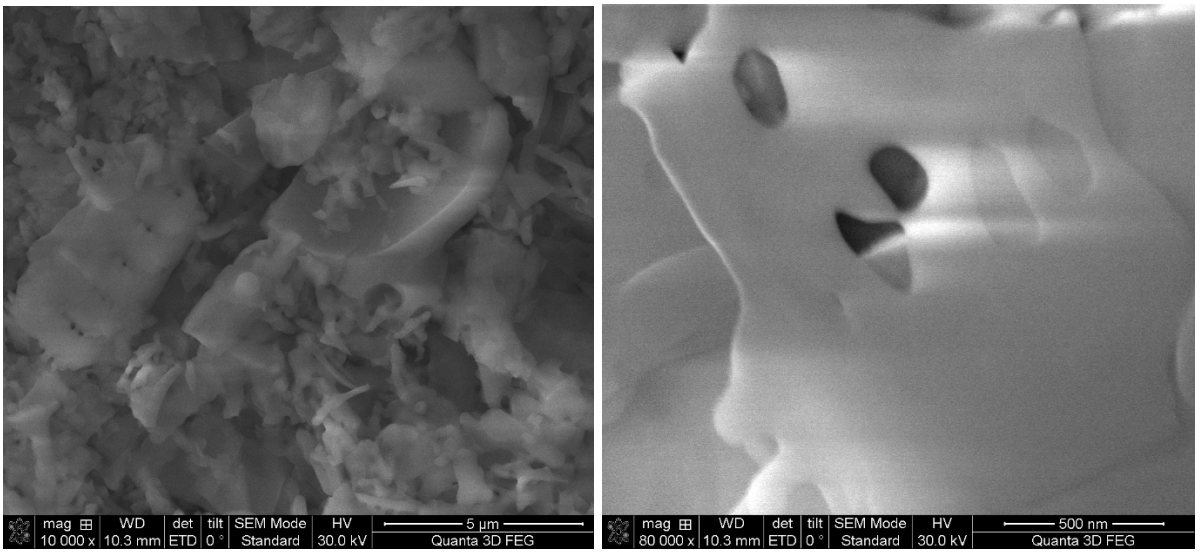

Figure 9: SEM of thermally treated sample.

4 Conclusions

From the physical-mechanical point of view, trepel represents a porous sedimentary rock (of biogenetic origin) with grayish to grayish-white color, soft and very light, with fine to superfine grained structure. The bulk density of trepel is 0.60 – 0.68 g/cm^3, the density amounts 2.41 g/cm^3, the compressive strength in natural state (raw) is 3.45 MPa, while the total porosity is from 67-71%. According to the chemical composition, it can be concluded that trepel represents acidic rock with a dominant presence of silica at 63.51%. The mineralogical characterization revealed the presence of the following minerals: quartz, plagioclase, muscovite and chlorite. Maintaining the 800°C temperature for a period of 1 hour significantly decomposed the present feldspars. The thermal treatment at 1000°C results in the formation of mullite, which is unusual to form at this temperature. However, its appearance is prescribed to the high reactivity of trepel (the super fine particles and the presence of the amorphous phase). Further temperature increase up to 1200°C, majorly increased the mullite phase with simultaneous increase of the amorphous phase followed with the appearance of tridymite.

SEM shows globular forms of quartz, skeletons from diatomae algae and other forms of clay minerals; whereas the thermally treated samples show morphological changes followed by the decrease of the size of the pores in the raw material. The reduction of the pores makes this materials suitable for filtration purposes.

Based on the abovementioned results, it can be concluded that at significantly lower temperatures, due to the appearance of mullite as binding component which enables high mechanical properties, trepel can be used as basic raw material for obtaining various types of ceramic materials (construction materials and various thermal insulating materials), various types of zeolites, waterglass, amorphous SiO_2 etc.

Conflict of interest: Authors declare no conflict of interest.

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