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Hydrothermal Reaction of Trepel with $Ca(OH)_2$

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INTRODUCTION

Inorganic, non-metallic, raw materials are suitable for various applications. Silicon dioxide (also known as silica) is a widespread in nature and it occurs in various forms [1-4].

Trepel is form of silica (SiO_2) derived either from thedecomposition or alterations of chert or as a residual product fromthe decomposition of a highly siliceous limestone.Diatomite or diatomaceous earth (also known as tripolite,kieselguhr, infusorial earth) is a hydrous or opalescent form of silica[5]. Trepelis a natural mixture of diatomite and clay minerals [6]. It's a typical sedimentary rock of biogenetic origin, with greyish-white color,weakly bound, soft (1-2 by Mohs) and very light, porousmaterial [7].

Trepel is a suitable raw material for production of ceramic products, for synthesis of zeolites, as absorbent for cleaning of raw industrial waters etc [8-12]. In this paper the aim is to use trepelas raw material for production of porous ceramicproducts.

RESULTS AND DISCUSSION

In this paper, the following materials were used as starting materials:

- Trepel from the Brod-Gneotine (Bitola region, Republic of Macedonia), and
- Calcium hydroxide (product of SIGMA)

Physical examinations of trepel

The physical properties of the examined trepel are shown in table 1, while a macroscopic picture of the raw material (trepel) is shown in figure 1.

Table 1. Physical properties of trepel from Brod-Gneotino

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

Figure 1. Raw trepel from Brod-Gneotino

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

Table 2. Chemical analysis of trepel form Brod-Gneotino

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
Na2O	2.33
SO3	0,.69
LOI	9.60
Total	99.77

XRPD examination of trepel

X-ray powder diffraction (XRPD) 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).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. Results of the XRPD examination are shown in Fig. 2.

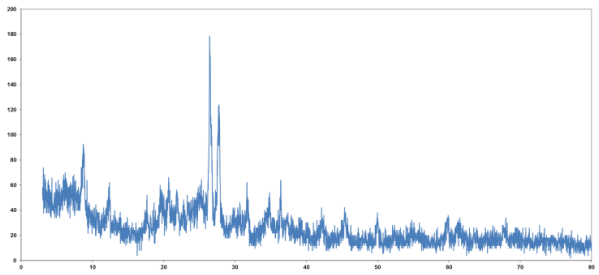

Figure 2. XRPD spectra of trepel from Brod-Gneotino

Microscopic examinations of trepel

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.

The SEM examinations confirm the results of the polarizing microscopy. Alga Diatomeae are shown on the SEM-pictures (fig. 3) resembling disks of sunflower with or without peripheral ends. 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.

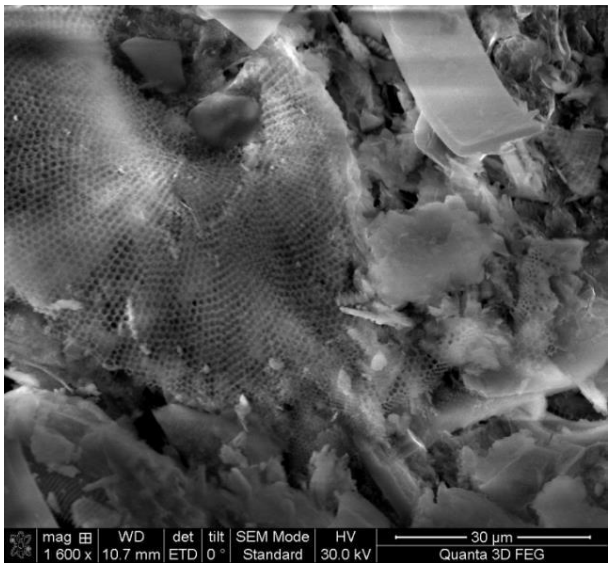

Figure 3. SEM of trepel (microfossil-diatomite)

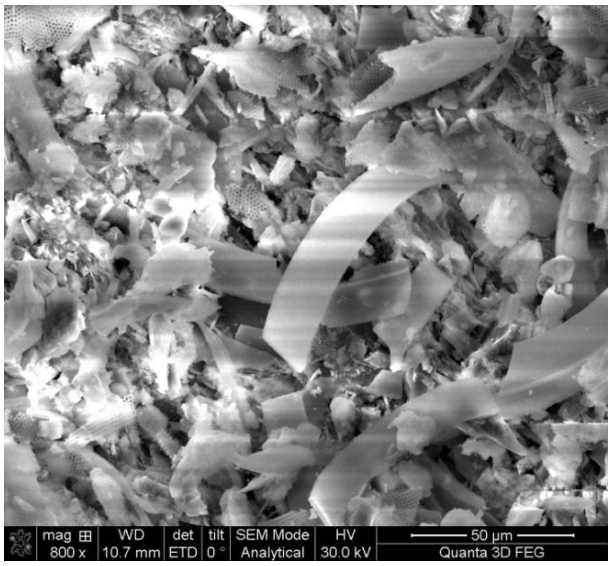

Figure 4. SEM of trepel mass composed of microrelics – opal globules of biogenetic origin

Thermal examinations of trepel

Differential-thermal and thermo-gravimetrical (DT/TG) 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.

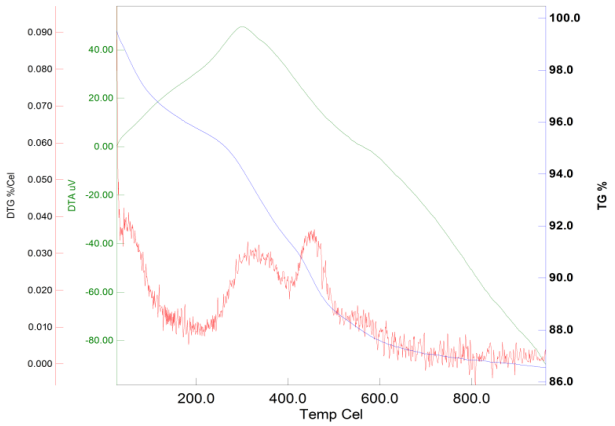

Figure 5. DTA/TGA examinations of trepel

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 curveevident 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.

FTIR examinations of trepel

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

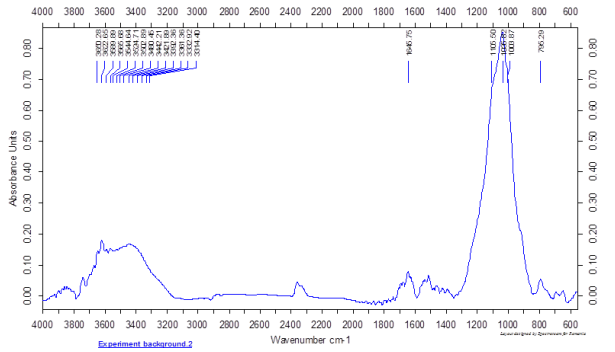

Figure 6. IR spectra of trepel from Brod-Gneotino

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.

Sample preparation

A homogenous mixture of 80 % trepel and 20 % calcium hydroxide was prepared. The probes were obtained with a cylindrical mold and were pressed on a mechanical press at 2 MPa and 10 MPa. Further on, the probes were hydrothermally treated at 130 °C for a period of 3 hours. Upon autoclaving the probes were first dried at constant mass, and then their physical-mechanical properties were determined.

Figure 7. Hydrothermally treated probes (3 hrs, 130°C)

Physical-mechanical properties of products

The following physical-mechanical analyses were performed on the ceramic products obtained from the hydrothermal synthesis (autoclaved in period of 3 hours at 130 °C): bulk mass, porosity and compressive strength.

Results of the physical-mechanical analyses of the products obtained during the hydrothermal treatment (130 ºC for 3 hours)are shown in table 3.

Table 3. Physical-mechanical properties of products

Property	Value
Bulk density	0.85 g/cm^3
Total porosity	61%
Compressive strength (prepared at 2 MPa)	5.14 MPa
Compressive strength (probes prepared at 10 MPa)	22.54 MPa

XRPD examinations of product

The results of the XRPD examination of the product obtained upon the hydrothermal treatment at 130 °C for a period of 3 hours is shown in figure 8.

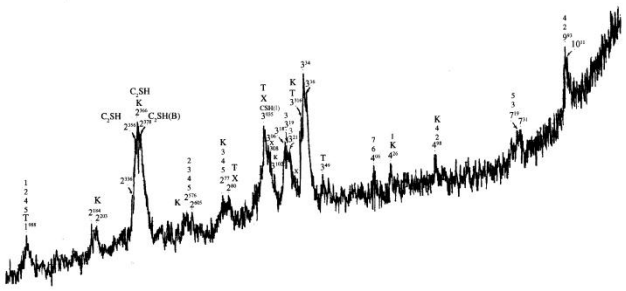

Figure 8. XRD of product(X= xonolite, T= tobermorite, 1= quartz, 2 = feldspar, 3= ilite, 4= mulite, 5= tridymite)

Based on the results obtained from the XRPD examination, it's evident that during the hydrothermal treatmentnew phases are formed and are clearly seen on the XRPD diffractogram.

Infra red examinations of product

The results of the infra red examinations of the product obtained during the hydrothermal treatment at 130 °C for a period of 3 hours is shown in figure 9.

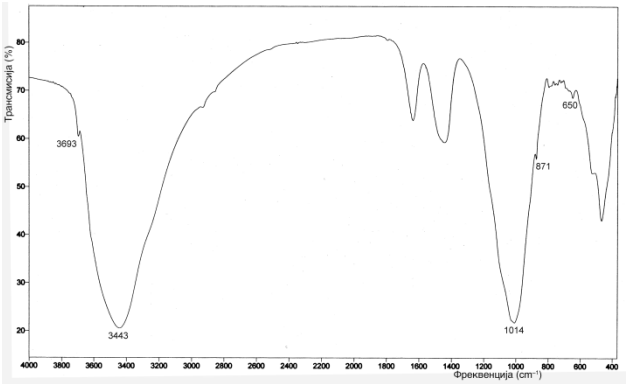

Figure 9. IR spectra of product

As showed in fig. 9, the main Si-O band at 1014 cm^{-1}is due to substitution of the Si^{4+} ion in the tetrahedral position with three valent ions. The absorbtion band on the region form 3400 to 3700 cm^{-1} is due to the presence of OH groups.The bands at 3450 cm^{-1} and 1630 cm^{-1}are as result of the new phase tobermorit present in the sample. The band at 640 cm^{-1} is due to the presence of monocalcium silicate hydrate CSH(I).

DTA/TGA examinations of product

The results of the thermal examinations of the product obtained during the hydrothermal treatment at 130 °C for a period of 3 hours is shown in figure 10.

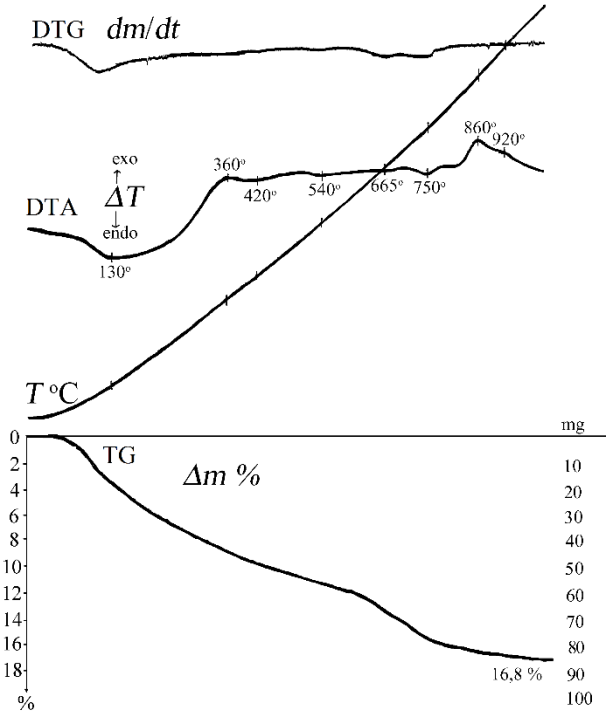

Figure 10. DTA/TGA examinations of product

The differental-thermal analysis and the thermo-gravimetric analysis of the product show the following results:

- the wide endothermic peak at 130 °C is due to the dehidratation of the mass
- the exothermic peak at 360 °C is due to the crystallization of the initial mass
- the small endothermic peaks at 420 and 540 °C are due to the presence of C_2SH (A) - hilldebrandit in the sample
- the endothermic peak at 665 °C is due to the presence of tobermorite in the probe
- the endothermic peak at 750 °C is due to the presence of C_2SH (C)– dicalcium silicate hydrate phase
- the exothermic peak at 860 °C is as result of the crystallization of CSH(B) into wollastonite.

CONCLUSION

Based on the results shown in the previous section it can be concluded that during the hydrothermal treatment of the samples prepared with 80% trepel and 20% calcium hydroxide, new phases are formed. These newly formed calcium silicate hydrates (mainly tobermorite, xonotlite and gyrolite) reflect in the

increased physical-mechanical characteristics of the obtained products. Products have total porosity of 61% and compressive strength over 5 MPa (5.14 MPa and 22.54 MPa).

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