278
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PHYSICAL-CHEMICAL AND MINERALOGICAL-PETROGRAPHIC EXAMINATIONS OF DIATOMITE FROM DEPOSIT NEAR VILLAGE OF ROŽDEN, REPUBLIC OF MACEDONIA

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A b s t r a c t: For the characterization of the natural amorphous SiO_2 found in a new deposit in Republic of Macedonia, the following examinations were performed: physical-mechanical, chemical, mineralogical, SEM, IR and thermal examinations. Physical-mechanical analyses show that it is a white to grey colored rock, of low hardness, with a low volumetric mass and high porosity. Chemical analyses show that the material dominantly contains SiO_2. Mineralogical and XRD analyses show high percentage of isotropic amorphous mass content, with minimal contents of submicroscopic cryptocrystalline mass. Thermal analyses show high thermal stability. Based on the conducted research of the raw material from the new deposit, it can be concluded that it represents SiO_2-diatomite of high quality, useful for various purposes.

Key words: amorphous SiO_2; diatomite; thermal analysis; chemical analysis; XRD analysis; optical microscopy; SEM analysis

INTRODUCTION

Inorganic raw materials are suitable for various uses. Silicon dioxide, also known as silica, is widespread in nature and it occurs in various forms [1–4]. Macedonia is rich in amorphous SiO_2 materials, and these materials have a wide spectrum of potential use and application [5, 6]. In this paper the aim is to characterize in details the raw material from Rožden (Kavadarci region) and determine its application. The exploitation process of the raw material would be surface-based; this is due to the fact that the humus thickness is only about 30 to 40 cm over the raw material.

Fig. 1. Geographical map of the deposits

EXPERIMENTAL

Macroscopic examination

The tested sample probe is pretty loose and soft, weak rock with white to greyish white color. The sample probe is characterized by a low bulk density which is less than 1 g/cm^3. The probe is easily disintegrated by applying pressure to it; however, the fine particles give you the feeling of scratch.

Fig. 2. Macroscopic sample of the raw material

Physical-mechanical examinations

The characterization of the physical-mechanical properties of the raw material is performed by analyzing the compressive strength in dry state, as well as for samples heated at 1000°C for a period of one hour. The bulk density of the raw material is determined in dry state as well as for samples heated at 1000°C for a period of one hour. The values of these analyses as well as the porosity and the density of the raw material are shown in Table 1.

Chemical silicate analysis

The chemical composition of the raw material is determined by classical chemical silicate analysis. The content of SiO_2 is determined gravimetrically, while the contents of Al_2O_3, Fe_2O_3, TiO_2, CaO, MgO and MnO are determined by volumetric analysis. The contents of the alkaline oxides K_2O and Na_2O are determined while using a flame photometer. Loss on ignition (LOI) is determined by thermal treatment of the sample at temperature 1000°C. The results of the chemical analyses are shown in Table 2.

T a b l e 1

Physical-mechanical properties of the raw material

Property	Value
Compressive strength	
In dry state	2.70 MPa
Heated at 1000°C	3.68 MPa
Bulk density in dry state	0.58 g/cm^3
Heated at 1000°C	0,60 g/cm^3
Porosity	
Open porosity	59.55 %
Closed porosity	12.08 %
Total porosity	71.63 %
Density	2,08 g/cm^3

T a b l e 2

Chemical composition of the raw material

Oxides	Mass (%)
SiO_2	92.97
$Al2O_3$	1.52
Fe_2O_3	0.21
TiO_2	0.06
CaO	0.43
MgO	0.19
MnO	0.01
SO_3	0.05
P_2O_5	0.09
K_2O	0.26
Na_2O	0.08
LOI	3.86
Total	99.73

The chemical analysis confirms the high purity of the raw material and the dominant presence of SiO_2 with about 93%.

The content of certain trace elements of diatomite are determined by ICP-MC analysis, and the results are shown in Table 3.

According to the presented results of the physical-mechanical and chemical examinations, the raw material can be classified as diatomite of the type 1 (for 70–80% SiO_2, according to *British Standard Specification*, BS 1795:1976) [7].

T a b l e 3

Results of ICP-MS analysis of the raw material

Elements	ppm
Ag	<1
As	<5,0
Bi	<10
Cd	<1,0
Co	1,0
Cr	5,3
Cu	9,3
Fe	1449
Hg	<10
Mn	33
Mo	<1,0
Ni	<1
P	<187
Pb	5
Sb	<10
Sn	<10
Zn	4,5

Mineralogical-petrographic analysis

It is evident from the mineralogical-petrographic examinations of the raw material, that the material dominantly contains isotropic sub-microscopic cryptocrystalline mass, most likely composed of opal which is the main mineral component. In the basic mass manifestations of amorphous components can be clearly noticed, as well diatomite, spongolite and other microfossils.

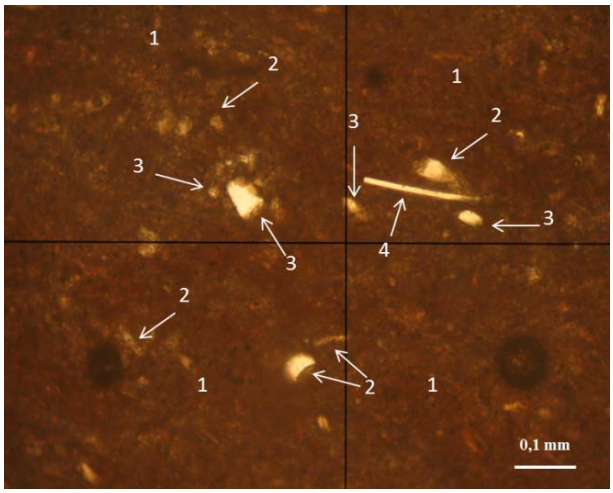

Fig. 3. Transmission optical microscopy – (1) isotropic mass, (2) diatomite, (3) fine sized quartz, (4) spongolite

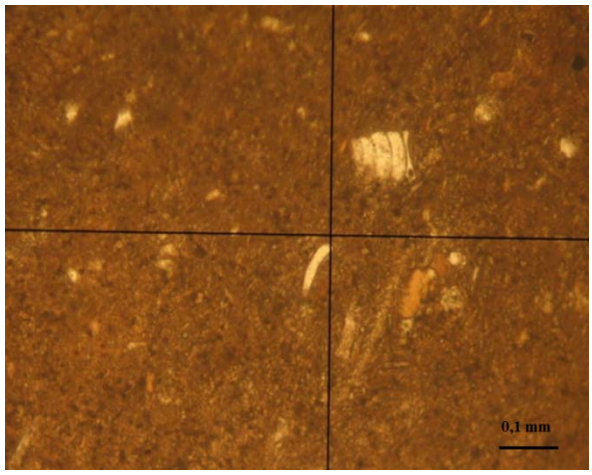

Fig. 4. Transmission optical microscopy – relics of snails with cone shape

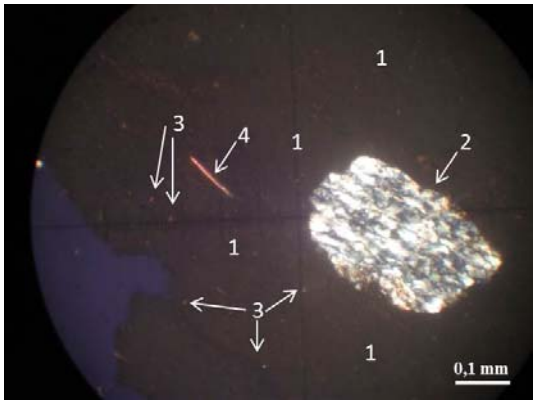

Fig. 5. Transmission optical microscopy – (1) amorphous mass, (2) quartz-slate, (3) quartz, (4) spongolite

In the isotropic mass, besides the various forms of relicts, there are super fine grains encountered. These grains can reach sizes up to 20-30 μm, and they represent alutogenic mineral component.

Scanning electron microscopy analyses

The results of the scanning electron microscopy provide the following data: presence of various skeletal shapes and their morphological characteristics, skeletons of microorganisms which have clearly visible pores and canals. In the macro-level the porosity of the raw materials can be defined as homogenous. The microstructural analysis also shows that the pores are of various sizes, shapes and volume. Majority of the pores are open and do not contain impurities. The dimensions of the nanopores are in the range 300–600 nm, and they make this material usable in various fields. Thus, the raw material can be used as natural filter, as adsorbent, as clarifier in the food industry [8, 9].

Fig. 6. SEM of the diatomite

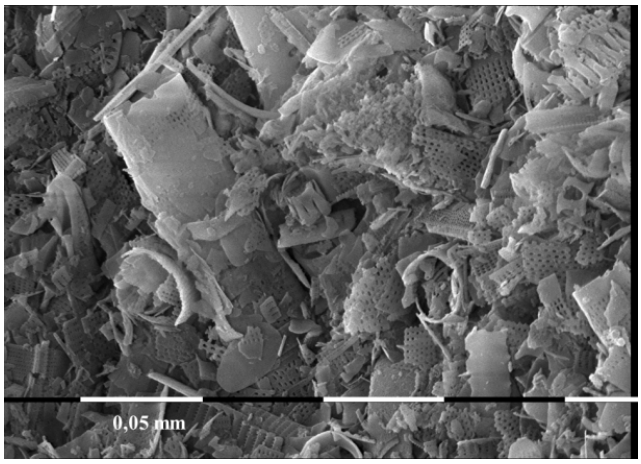

Fig. 7. SEM of the diatomite

X-ray examinations

The crystalline phases of the diatomite are determined by XRD analysis. XDR 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 the natural raw material are presented in Figure 8.

Based on the results of the XRD analysis, it can be concluded that the examined raw material is amorphous. A small wide peak on the diffractogram in the area 19–25 ° 2θ, is the interval for the crystalline modifications of SiO_2, quartz, cristobalite and tridymite.

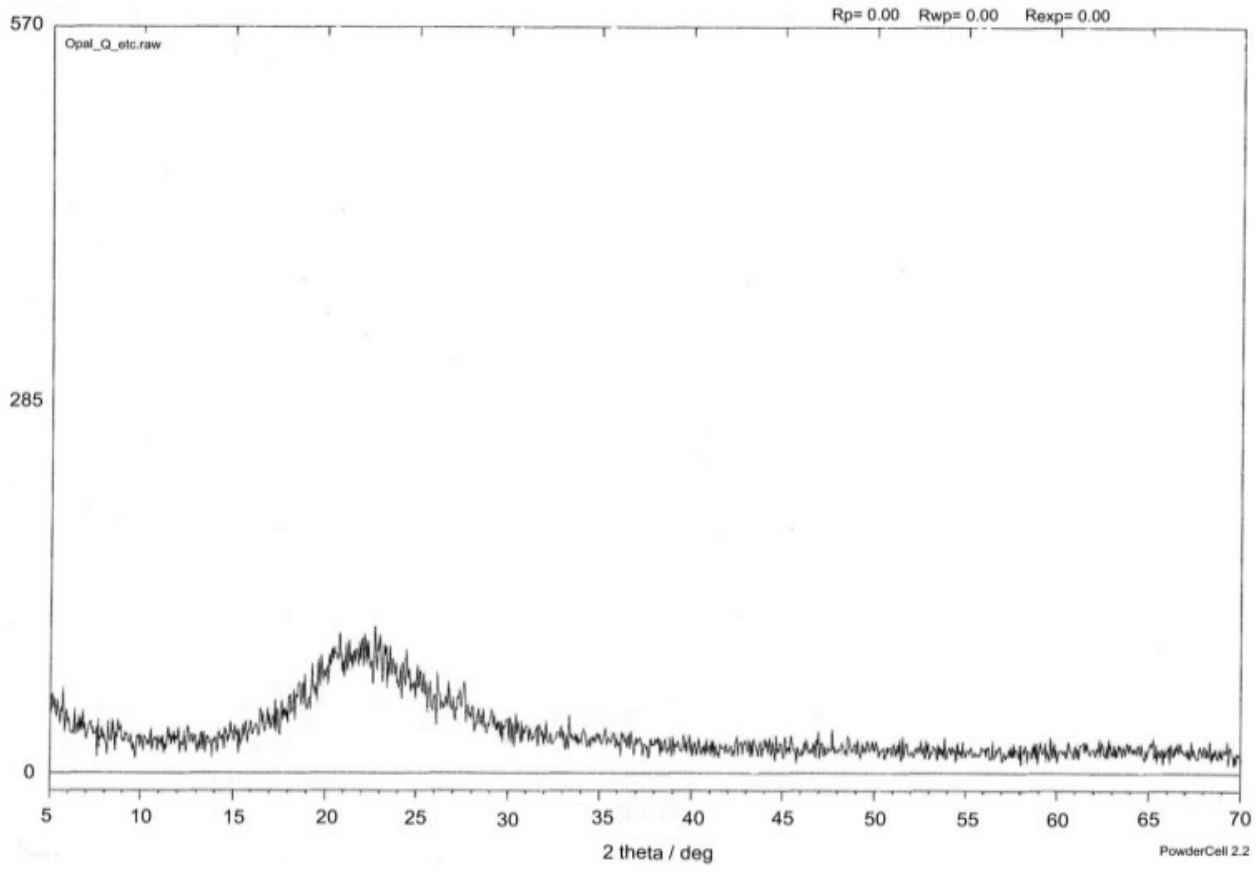

Fig. 8. XRD analysis of the diatomite

DTA/GTA analyses

DTA/TGA analyses of the diatomite were performed with Stanton Redcroft, England – apparatus, under the following experimental conditions: temperature range 20 – 1200 °C; speed of heating 10 °C/min; sample mass 11,7 mg; gas environment – air; material carrier – ceramic pot. Results of the differential-thermal analysis and the thermo-gravimetrical analysis of the diatomite are shown in Figure 9.

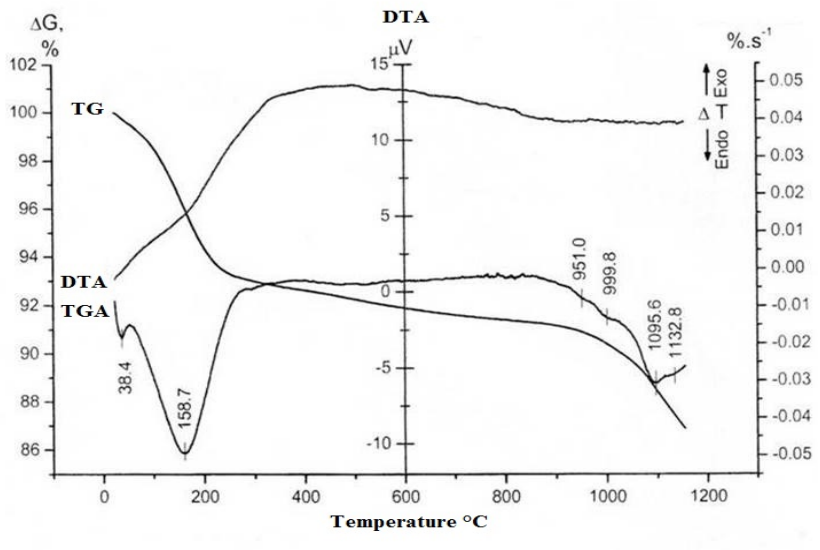

Fig. 9. DTA/TGA of diatomite

Thermo-gravimetrical analysis shows an intensive loss in weight in the temperature interval 30–200 °C and 900–1200 °C. The first phase of the endothermic peak at 158°C is due to loss of the absorbed water from the surface and the open pores, while the intense loss of mass during the second phase at the temperature range 900–1200 °C is as result of loss of the hydrated water. DTA/TGA confirms that the material does not crystallize even after a thermal treatment at 1000°C, i.e. it remains amorphous material.

FTIR spectroscopy

FTIR spectroscopy was performed in order to examine the way of connecting hydroxyl groups on the surface of the diatomite. Figure 10 shows the results of the IR spectroscopy of the diatomite.

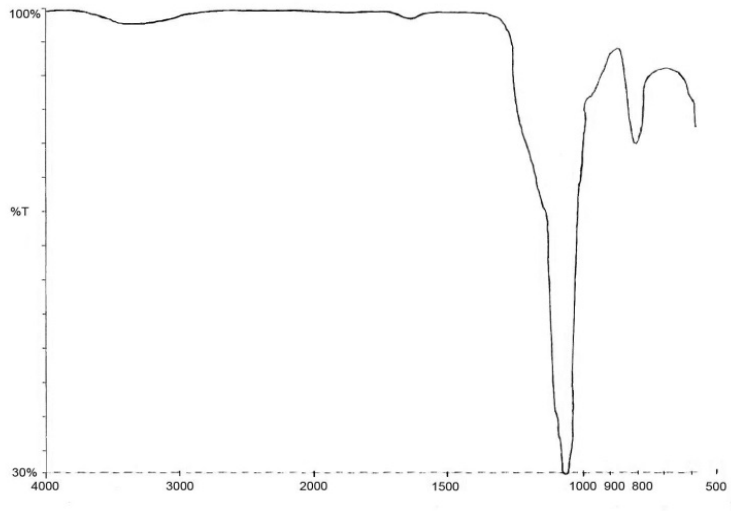

Fig. 10. IR spectroscopy of diatomite

CONCLUSION

Based on the detailed examination of the natural amorphous SiO_2 from the new deposit in Republic of Macedonia, the following can be concluded that the natural amorphous SiO_2 is weakly bound, soft loose rock with a white to greyish white color; it has a low bulk mass and high porosity. XRD analyses show that the material is in amorphous state. DTA and TGA analyes point characteristic hydroxyl and crystal-hydrate groups, important parameters especially for application in processes where surface characteristics are of primary importance. IR spectroscopy confirms and deepens the findings for the connected water and the hydroxyl groups of the DTA/TGA with the characteristic absorption strips of an amorphous SiO_2. With the microscopic examination the origin of the material is defined. The material represents isotropic sub-microscopic cryptocrystalline mass of diatomite, spongolite and microfossils, with a small percentage of mineral impurities of optical anisotropic character. The chemical analysis of the raw materials shows high percentage of the basic component SiO_2. From chemical as well as mineralogical point of view, the raw materials represents a high quality natural amorphous SiO_2-diatomite which can be compared with the other well world known deposits. Based on the results, the raw material from new deposit near Rožden can find usage in several industrial branches: construction ceramics, refractory ceramics, special oxide ceramics, as well as widespread use as means for filtering, adsorbent, catalysts, etc.

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Р е з и м е

ФИЗИЧКО-ХЕМИСКИ И МИНЕРАЛОШКО-ПЕТРОГРАФСКИ ИСПИТУВАЊА НА ДИЈАТОМЕИТЕ ОД НАОЃАЛИШТЕТО ВО БЛИЗИНА НА СЕЛОТО РОЖДЕН, РЕПУБЛИКА МАКЕДОНИЈА

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Клучни зборови: аморфен SiO_2; дијатомеи; термичка анализа; хемиска анализа; XRD-анализа; оптичка микроскопорија; SEM-анализа

За карактеризација на аморфна SiO_2-суровина од ново наоѓалиште во Р. Македонија се реализирани физичко-механички, хемиски, минералошки, SEM, IR и термички испитувања. Суровината претставува бело-сивкаста карпа со ниска тврдост, мала волуменска маса и висока порозност. Хемиската анализа покажува дека материјалот доминатно содржи SiO_2. Минералошките и XRD анализите покажуваат висок удел на изотропна аморфна маса во составот со минимални содржини на субмикроскопска криптокристална маса. Термичката анализа покажува висока термичка стабилност на материјалот. Од реализираните испитувања на SiO_2-суровина од новото наоѓачиште, може да се заклучи дека SiO_2-диатомеите се со висок квалитет, со можност за широка примена.