JU ZAVOD ZA GEOLOŠKA ISTRAŽIVANJA CRNE GORE
GEOLOGICAL SURVEY OF MONTENEGRO

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Dragan S. Radulović[1] , Darko Božović[2], Jovica Stojanović[1], Vladimir Jovanović[1], Dejan Todorović[1], Branislav Ivošević[1], Sonja Milićević[1]

INVESTIGATION IN ORDER TO DEFINE THE TECHNOLOGICAL PROCESS OF OBTAINING FILLERS FOR USE IN VARIOUS INDUSTRIES ON THE BASIS OF LIMESTONE “GLAVATSKE KUĆE”-KOTOR

Abstract

This paper presents results of investigations of the possibility of using “Glavatske Kuće”-Kotor limestone (Montenegro) as filler in various industry branches. Micronization methods, granulometric composition, oil and water absorption and degree of whiteness were investigated, and chemical and thermal analyses (DT/TG) were performed. Physico-chemical properties of this limestone classify it among high quality carbonate raw materials with relatively high $CaCO_3$ content of 97.68 %, as well as low $MgCO_3$ content of 1.849 % and low silicate content (SiO_2 0.24 %). Its quality satisfies requirements of standards on using of calcium carbonate as filler in industry of paints and coatings; glass industry; foundry industry; sugar industry and metallurgy. Due to the low degree of whiteness (77,85 %) “Glavatske Kuće” limestone cannot be used in pharmaceutical and cosmetics industry, paper industry. Because of increased MgO content, limestone “Glavatske kuće” cannot be used in the fertilizers industry. Due to relatively high content of heavy metals, Cu (47 ppm), Ni (50 ppm) and Cd (8 ppm), as well as biogenic elements P_2O_5 (0.0234 %), K_2O (0,0157 %), “Glavatske Kuće” limestone cannot be used in production of cattle feed and for neutralization of acidic soils.

Key words: *limestone, filler, industrial use, standards, comminution and classification.*

[1] *Institute for technology of nuclear and other mineral raw materials, 86 Franchet d’Espery Street, Belgrade, Serbia, d.radulovic@itnms.ac.rs*

[2] *Geological Survey of Montenegro, Podgorica, Montenegro*

ISTRAŽIVANJE U CILJU DEFINISANJA TEHNOLOŠKOG PROCESA DOBIJANJA PUNILA ZA UPOTREBU U RAZLIČITIM INDUSTRIJAMA NA OSNOVU KRAČNJAKA "GLAVATSKE KUĆE"-KOTOR

Apstrakt

U ovom radu su prikazani rezultati istraživanja mogućnosti upotrebe krečnjaka „Glavatske kuće"-Kotor (Crna Gora) kao punila u različitim industrijskim granama. Ispitivane su metode mikronizacije, granulometrijski sastav, upijanje ulja i vode i stepen beline, izvršene su hemijske i termičke analize (DT/TG). Fizičko-hemijska svojstva ovog krečnjaka svrstavaju ga među visokokvalitetne karbonatne sirovine sa relativno visokim sadržajem $CaCO_3$ od 97,68 %, kao i niskim sadržajem $MgCO_3$ od 1,849 % i niskim sadržajem silikata (SiO2 0,24 %). Svojim kvalitetom zadovoljava zahteve standarda o upotrebi kalcijum karbonata kao punila u industriji boja i premaza; industrija stakla; livnička industrija; industrije šećera i metalurgije. Zbog niskog stepena beline (77,85 %) krečnjak „Glavatske kuće" ne može se koristiti u farmaceutskoj i kozmetičkoj industriji, industriji papira. Zbog povećanog sadržaja MgO, krečnjak „Glavatske kuće" ne može se koristiti u industriji đubriva. Zbog relativno visokog sadržaja teških metala, Cu (47 ppm), Ni (50 ppm) i Cd (8 ppm), kao i biogenih elemenata P_2O5 (0,0234 %), K_2O (0,0157 %), krečnjak „Glavatske kuće" ne može se koristiti u proizvodnji stočne hrane i za neutralizaciju kiselih zemljišta.

Ključne reči: Krečnjak, punila, industrijska upotreba, standardi, usitnjavanje i klasifikacija.

1. INTRODUCTION

The limestone is a sedimentary rock predominantly comprising carbonate minerals (i.e. calcium carbonate, $CaCO_3$) in the quantity that surpasses 50 %. Quartz and clay minerals (e.g. kaolinite, hydrous mica, montmorillonite) are other two major constituents of the limestone (Gunasekaran and Anbalagan, 2008; Radulović et al., 2017c). Since a substitution of calcium by magnesium occasionally occurs, a limestone that contains 5-35 % of Mg is defined as "magnesian limestone". If Mg content is below 5 %, the rock is classified as a "high-calcium limestone" (Radulović et al., 2017c; Dollimore et al., 1994). The carbonates present in the limestone customarily appear as calcite, aragonite and/or vaterite mineral phases. However, the only crystal form of real significance is calcite (Radulović et al., 2017c; Yoğurtcuoğlu and Uçurum, 2011).

Calcite ($CaCO_3$) is one of the most common minerals on Earth, comprising about 4% by mass of the Earth's crust (Radulović et al., 2017a). Calcite occurs in carbonates and nepheline syenites as the primary component of the magmatic phase, and is also common in hydrothermal deposits. In metamorphosed deposits, calcite occurs in form of marble. In carbonates, dolomite (Ca, Mg)CO_3, magnesite ($MgCO_3$), siderite ($FeCO_3$), rhodochrosite ($MnCO_3$) and smithsonite ($ZnCO_3$) occur as isomorphous with calcite (www.minweb.co.uk/carbonates/calcite.html).

By being the most abundant and enclosing at least 50% of all present mineral phases in the limestone, calcite is an important resource and subject of investigations in various scientific fields: mineralogy, chemistry, physics, materials science (Radulović et al., 2017c; Radulović et al., 2017a; Saeid and Elnaz, 2016; Weerdt et al., 2011; Felekoglu, 2007; Anastasiou et al., 2015). Calcite crystallizes rhombohedrally, in a hexagonal-scalenohedral class and space group R3c. The parameters of a single cell are as follows: a = b = 4.988 Å, c=17.061Å, α=β=90°, γ=120°, V= 367.85 $Å^3$, Z=6 (Radulović et al., 2017a; Yuan et al., 2008; Radulović, 2011; Przeniosło et al., 2016). Due to the perfect rhombohedral cleavage, calcite exhibits a small value of Mohs hardness (3.0). The specific gravity of calcite is 2.7 (Yoğurtcuoğlu and Uçurum, 2011; Radulović et al., 2017a). The thermally induced behavior, i.e. calcium carbonate stability constrains and the rules of phase transitions, represents a basis for a comprehensive study of the limestone (Radulović et al., 2017a; Przeniosło et al., 2016; McIntosh, 1990; Salvador, 1989).

Calcite is used for production of lime and Portland cement, while in construction industry it is applied as crushed or decorative stone. Calcium is also an important micronutrient. Several commercial drugs (antacids and calcium supplements) are, in fact, ground limestone (Radulović et al., 2017a; Barcina et al., 1997). Also of importance is its application as a filler, in various branches of industry (pharmaceutical, fodder, PVC and rubber, paints and glue industries, mineral fertilizers industry, foundry, metallurgy, etc.), as well as in agriculture where it is used for adjustment of soil pH value.

Republic of Montenegro has big reserves of limestone in coastal area and in south of the territory (William, 2011). Even though deposits are huge, limestone is mainly used in construction as construction stone, and to some extent as architectural stone (Radulović et al., 2017a; ITNMS report, 2011). Since calcium carbonate as filler is much more expensive than construction stone, relevant institutions of Montenegro initiated investigations of the possibility of using limestone as filler (Radulović et al., 2017a). On the basis of the obtained results it was evaluated whether it can be used as filler in accordance with standards (SRPS) in various industry branches (Radulović et al., 2017a; Radulović et al., 2017b; Terzic et al., 2017; Mihajlović, 2011; Sekulić, 2011).

“Glavatske Kuće”-Kotor deposit consists of carbonate sediments, mostly limestone ones, and less dolomitic sediments. Ore reserves are estimated at about 15,000,000 t of limestone (Radulović et al., 2017a; William, 2011). The aim of investigations presented in this paper was to determine the possibility of using raw material as filler in various industry branches.

2. EXPERIMENTAL

2.1. MATERIALS AND METHODS

Starting limestone sample used in investigations was from "Glavatske Kuće" - Kotor deposit. First, its specific volumetric weight (density) and granulometric composition were determined. Its density was measured by pycnometer with xylol as fluid, granulometric composition was determined by Tyler screen (http://minerals.usgs.gov/minerals/pubs/commodity/stone_crushed/mcs-2010-stonc.pdf). Granulometric composition of the micronized sample was determined by sieve size 63 µm, classification on Cyclosizer and Bach elutriator. Limestone filler quality was determined by chemical, mineralogical (XRD), DT/TG and FTIR spectroscopy analysis. Degree of whiteness was determined by whiteness meter, according to MgO 100% standard.

Mineralogical analysis of the limestone samples was conducted by means of the X-ray powder diffraction (XRD) technique. The X-ray powder diffraction patterns were acquired on a Philips PW-1710 automated diffractometer using a Cu tube operated at 40 kV and 30 mA. The instrument was provided with a diffracted beam curved graphite monochromator and a Xe-filled proportional counter. Measurements were conducted at ambient temperature (25^{o}C). The diffraction data were assembled in the 2θ Bragg angle range from 5 to 70°, counting for 1 s (qualitative identification) at every 0.02^o step. The divergence and receiving slits were fixed at 1 and 0.1, respectively.

The thermal behavior was monitored by simultaneous Differential thermal analysis (DTA) and thermo-gravimetry (TG) in the temperature range from 20^o C to 1000^o C. DTA/TG analyses were conveyed in a static air flow by an automatic thermo-analyzing system: STA 409EP (Netzsch, Germany). The limestone samples (100 mg) were loosely packed into an alumina holder and thermally treated under a nitrogen atmosphere at a heating rate of 10° C/min, in temperature interval from 20 to 1000° C.

The chemical bonds, distinctive molecular fingerprints, functional groups and covalent bonding information were detected via Fourier Transform Infrared (FTIR) spectroscopy analysis. The FTIR spectra were obtained on a Nicolet IS-50 spectrometer (Thermo Fisher Scientific, USA), recorded in KBr transmission mode in the 4000-400 cm-1 range and 32 scans at resolution 4.

The morphology of the samples was characterized by scanning electron microscopy (JEOL JSM–6610LV). The investigated samples were covered by gold using a sputter machine type BALTEC-SCD-005 for improvement of the conductivity prior to imaging.

2.2. INVESTIGATION OF PHYSICAL PROPERTIES OF STARTING SAMPLE

Specific volumetric weight of the starting sample is γ= 2,689 g/cm^3.

Based on the results of screening test, is drawn a diagram of particle size distribution, shown in Figure 1, for samples of limestone "Glavatske Kuće". In Figure 1, shows the direct curve of particle size distribution and cumulative curves and average sample of outflow and flow limestone deposits "Glavatske Kuće"-Kotor. From the intersection of cumulative curves average outflow and flow determined that the average diameter of the sample of limestone d_{50} = 9.06 mm, and upper size limit of the sample was d_{95}=18.54 mm.

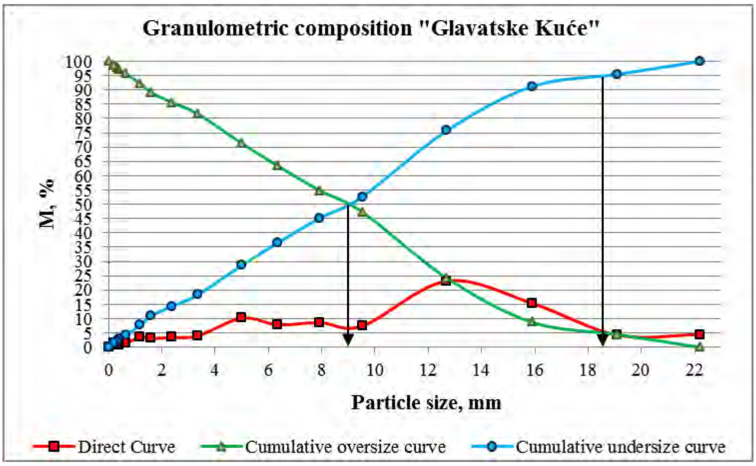

Figure 1. The curves of particle size-composition of the starting sample ""Glavatske Kuće"" - Kotor

2.3. TECHNOLOGICAL INVESTIGATIONS

For investigations of the possibility of using limestone as filler in various industry branches limestone was micronized, and thus obtained product were subjected to the following physico-chemical characterization:

- chemical analysis, mineralogical analysis (XRD), thermal (DT/TG) analysis, Fourier Transform Infrared (FTIR) spectroscopy analysis, morphology of the samples by scanning electron microscopy (SEM), determination of granulometric composition, degree of whiteness and absorption of oil and water.

2.3.1. Determining granulometric composition of micronized sample

Table 2. Granulometric composition of grinded sample "Glavatske Kuće"

Size class [µm]	M, %	↑ΣM, %	↓Σ M, %
-63+44	3,20	3,20	100,00
-44+33	8,50	11,70	96,80
-33+23	7,90	19,60	88,30
-23+15	5,50	25,10	80,40
-15+11	5,00	30,10	74,90
-11+5,7	42,78	72,88	69,90
-5,7+0	27,12	100,00	27,12
Input	100,00	/	

Granulometric composition of the micronized products showed that the finest class -5.7 µm content is around 27%.

2.3.2. Chemical analysis

Results of chemical analysis of the micronized limestone with contents of main components and damaging components are presented in Tables 3. and 4.

Table 3. Chemical composition of main components of limestone sample

Comp.	CaO	$CaCO_3$	CO_2	MgO	Fe_2O_3	Al_2O_3
Cont., %	54.73	97.68	43.92	0.884	0.065	0.0090

Comp.	SiO_2	K_2O	Na_2O	TiO_2	P_2O_5	LOI
Cont., %	0.240	0.0157	0.060	<0.02	0.0234	44.28

Table 4. Chemical composition of damaging components of limestone sample

Comp.	Cu	Mn	S	P	Ni	Cr	Mo
Cont., %	47ppm	26ppm	<0,01%	0,0102	50 ppm	10 ppm	<50 ppm

Comp.	Sb	Pb	Cd	pH	Fe solu.	As	Hg
Cont., %	<25 ppm	<25 ppm	8 ppm	9,50	0,043%	/	/

Results of physico-chemical characterization of "Glavatske Kuće" limestone sample and the required filler quality (Standards) lead to conclusion that this limestone is of good quality. Namely, its $CaCO_3$ content is high - 97.68 %, and MgO (0.884 %) and silicates (SiO_2 0.24 %) content low. However, relatively high content of heavy metals was found, above all Cu (47 ppm), Ni (50 ppm) and Cd (8 ppm) and biogenic element P (0.0102 %).

2.3.3. Determining mineralogical composition of micronized sample

2.3.3.1. H-ray diffraction studies

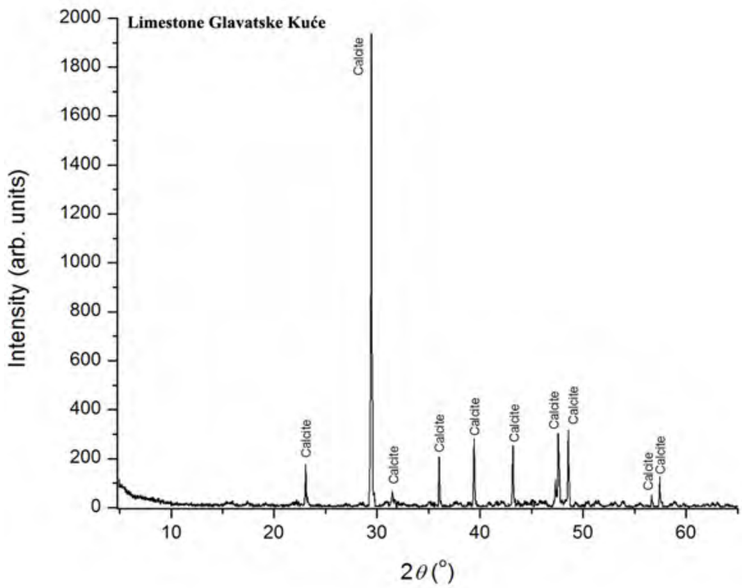

Figure 2. XRD diffractogram of "Glavatske Kuće" limestone sample

The XRD diagram indicate that the investigated limestone sample are mainly composed of calcite with minor amounts of dolomite, quartz, mica, and clay minerals. The minor phases can scarcely be distinguished on the diagram because their reflections are either too feeble or overlapped and superposed by other more significant peaks. In investigated sample, the calcite was found to be the most abundant; therefor the most significant XRD reflections belong to this mineral phase. According to the chemical analysis of the sample (Table 3), the content of calcium carbonate was 98.05%. The intensity of the calcite XRD peaks (very high the calcite peak of limestone situated at 30^o), indicates a high level of crystallinity and presence of less amorphous solid.

2.3.3.2. Infrared (FTIR) spectroscopy analysis

The FTIR measurements were conducted in the wide region of 4000-400 cm-1. The free carbonate ion belongs to the symmetry point group D3h. Therefore, the CO32- ion has four normal vibrations of which one belongs to the species A'1, one is of species A'2, while two vibrations belong to the E' species (Radulović et al., 2017c; Radulović et al., 2017a; Milosavljević, 1974). The carbonate functional group that is present in the calcite corresponds to the D3h point group as a nonlinear with 4 atoms (N=4). This group has 3N-6=6 basic vibrations of which N-1=3 are valent

(Radulović et al., 2017c; Radulović et al., 2017a; Milosavljević, 1974). The spectral difference between the more common groups may be related to crystal structure. The spectral relationships among the minerals of several groups are not well known, due to the complicated composition and crystal structure. Infrared active groups of CO_3, HCO_3, H_2O and OH normally dominate the absorption characteristics (Radulović et al., 2017c; Radulović et al., 2017a; Andersen and Brečević, 1991).

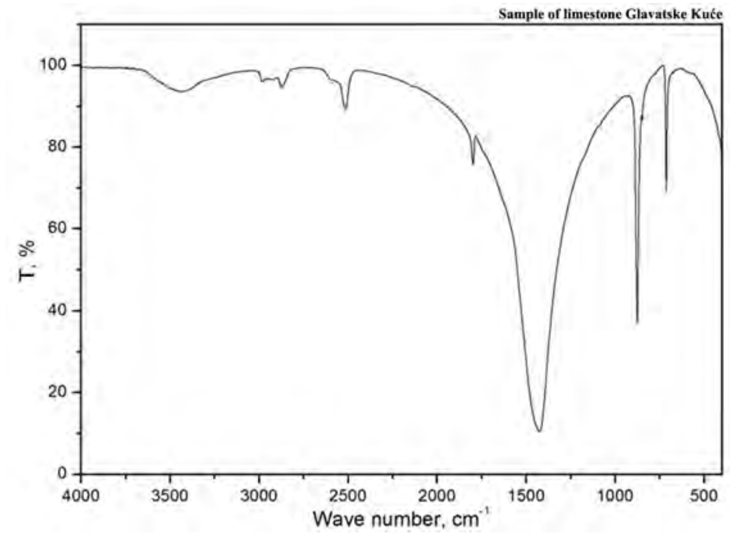

Figure 3. FTIR spectra of the "Glavatske Kuće" limestone sample

In the FTIR spectrum of the calcium carbonates ($CaCO_3$) the main absorption bands appear in the regions 1500-1400 cm^{-1}, 1100-1000 cm^{-1}, 900-800 cm^{-1} and close to 700 cm^{-1} (Radulović et al., 2017a; Andersen and Brečević, 1991). The infrared spectra of the calcite and dolomite groups are normally characterized by three prominent absorption maxima and two minor peaks (Radulović et al., 2017c; Radulović et al., 2017a; Andersen and Brečević, 1991). The analysis of the K19 sample showed eight peaks of different intensities on the diagram (given in Fig. 8): 3435, 2182, 2874, 2515, 1798, 1424, 876 and 712 cm^{-1}. The FTIR bands at 1424, 876 and 712 cm^{-1} had distinguished peaks, while the rest of peaks were minor. The registered bands are all considered to be caused by the CO_3 groups with the crystals (Radulović et al., 2017c; Radulović et al., 2017a; Huang and Kerr, 1960). Namely, from the analysis of the space group characteristics, the existence of four molecular frequencies for the CO_3 ions in calcite is acknowledged of which three are active in the infrared spectrum (Radulović et al., 2017c; Radulović et al., 2017a; Andersen and Brečević, 1991; Huang and Kerr, 1960; Hopkins et al., 2015).

Since the $CaCO_3$ contains less than one molecule of water per $CaCO_3$ in the structure (Radulović et al., 2017c; Radulović et al., 2017a; Andersen and Brečević, 1991), the bands that correspond to the three normal vibrations of the water molecule were found: at 3435, 2182, 2874 and 2515 cm^{-1} (antisymmetric and symmetric O-H stretches), and at 1798 cm^{-1} (HOH bending). The band of medium intensity observed at 876 cm^{-1} is assigned to the υ_2 which is a symmetric normal vibration of carbonate ion that corresponds to the CO_3 out-of-plane deformation mode. The strong broad bond at 1424 cm^{-1} region corresponds to the symmetric normal υ_3 vibration that is an asymmetric C-O stretching mode. A relatively weak absorption at 700 cm^{-1} can be related to the $\upsilon4$ vibration which is characterized by in-plane deformation mode. As it can be seen in Fig. 6, the acknowledged bands are split and the band maxima is being observed at 1424, 876 and 712 cm^{-1}. Thereby, the site symmetry for CO_3^{2}- that is present in the limestone (i.e. calcite as the main phase) can be described as D_3 ($A_1(R)(\upsilon_1)$, $A_2(I)(\upsilon_2)$ and $E(I,R)(\upsilon_3, \upsilon_4)$) which is in agreement with the crystalline structure that can be determined via XRD measurements (Radulović et al., 2017c; Radulović et al., 2017a; Andersen and Brečević, 1991). Also, a frequency value of the infrared inactive fundamental υ_1 of calcite can be determined from the frequencies of two combination bands $\upsilon_1+\upsilon_3$ and $\upsilon_1+\upsilon_4$ observed at 2515 cm^{-1} and 1798 cm^{-1}, respectively, for the samples at low temperature, resulting in the average value 1088 cm^{-1} for υ_1 which is in agreement with the value that can be obtained from the Raman spectra of calcite (Radulović et al., 2017c; Radulović et al., 2017a; Huang and Kerr, 1960).

2.3.3.3. Scanning electron microscopic analysis

The sample Glavatske Kuće limestone, was submitted to the scanning electron microphotography to acquire finer observations of the sample's microstructure (Fig. 4).

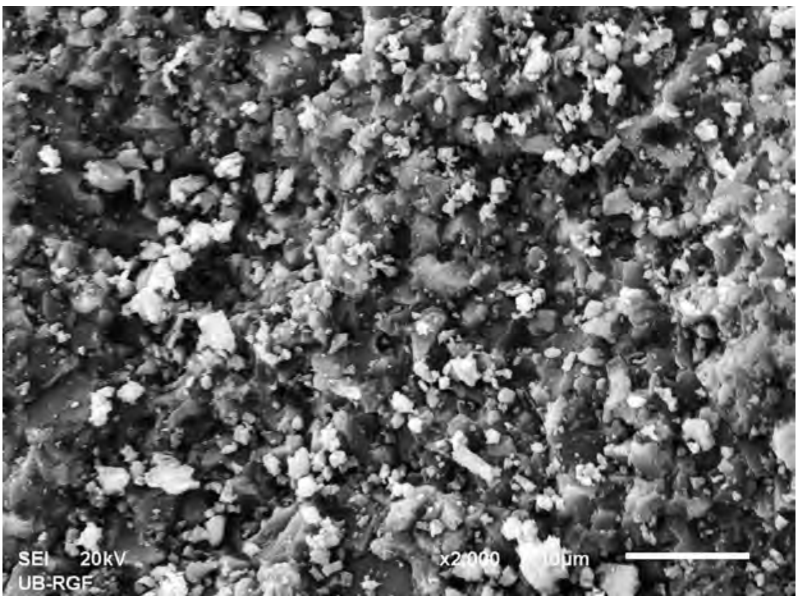

Figure 4. SEM microphotograph of the "Glavatske Kuće"- limestone sample

2.3.4. Determining the degree of whiteness

Whiteness was assessed on three samples of the limestone from deposit ""Glavatske Kuće"", and the result is shown in Table 5.

Table 5. The degree of whiteness the limestone samples

No	mark of the sample	whiteness according MgO– 100%
1.	"Glavatske Kuće"-1	77,95
2	"Glavatske Kuće"-2	78,15
3	"Glavatske Kuće"-3	77,45
	Average value	77,85

2.3.5. Determination of absorption water and oil

In order to determine absorption water and oil are also used three samples of the limestone from deposit ""Glavatske Kuće"", and the results are shown in Tables 6.

Table 6 Absorption of the oil of samples of limestone

No.	mark of the sample	absorption of the oil, %	absorption of the water, %
1.	"Glavatske Kuće"-1	13,45	16,95
2.	"Glavatske Kuće"-2	13,70	18,05
3.	"Glavatske Kuće"-3	13,65	17,35
	Average value	13,60	17,45

2.3.5. Thermal (DT/TG) analysis

Thermo-analytical methods are commonly applied in investigations of mechanisms and kinetics of solid state decomposition reactions. The shape of a DTA and/or TG curve is a direct function of the kinetics of reactions that take place within material, and it is also interrelated with chemical and mineralogical characteristics of the limestone (Radulović et al., 2017a; Vagenas et al., 2003). The limestone thermal behavior was assessed by means of the analysis of thermo-gravimetric and differential thermal curves of the samples that originated from Glavatske Kuće deposits. The testing has been conducted under same controlled atmosphere (described in Chapter 2.) Results of thermal (DTA/TG) analysis of the micronized sample "Glavatske Kuće" limestone are presented as a diagram in Figure 5.

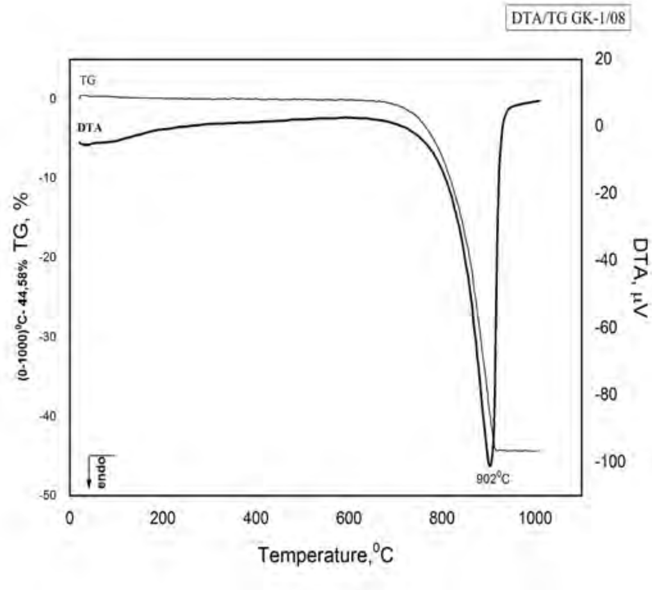

Figure 5. DTA/TG diagram of ”Glavatske Kuće” limestone sample

The dominant thermally induced reaction that took place in the investigated limestone sample, which contained over 90% of calcium carbonate, is calcination, i.e. decomposition of $CaCO_3$ induced by an exposure to strong heat. This reaction is important for the industrial application of limestone (Radulović et al., 2017c; Dollimore et al., 1994; Radulović et al., 2017a; Ersoy-Mericboyu et al., 1993).

The calcinations of the carbonate is an endothermic event, therefore a typical DTA curve for a sample of calcite rich limestone exhibits a single smooth decomposition step (Fig. 2). High-calcium limestone decomposes at temperatures in the vicinity of 800-900° C in one stage with the formation of calcium oxide and carbon dioxide. The dissociation proceeds gradually from the outside surface inwards, with the reaction taking place at an interface between calcite and the residual oxide (Radulović et al., 2017c; Dollimore et al., 1994; Radulović et al., 2017a). The shape of the endothermic peak with calcination temperature maximum at 902°C, is attributed to the decomposition of the calcite ($CaCO_3$) into CaO and CO_2, according to the following reaction:

$$CaCO_3 \rightarrow CaO + CO_2 \quad (1)$$

Immediately after this endothermic peak, DTA baseline does not drift neither endothermically nor exothermically, which means that there is no free lime present after the decomposition of calcite in the sample. The formation of the molten phase in the system did not appear in the applied thermal interval from 20° C up to 1000°C.

The TGA curves of the limestone (Fig. 2) showing only one peak of the mass variation due to completed thermal decomposition (phase transformation) of the calcium carbonate. The major mass loss takes place at approximately 900° C, and its value (measured in the temperature range from 650° C to 900° C) are 44.58 %. The value of the mass loss are in consistency with the obtained LoI.

3. RESULTS AND DISCUSSION

Limestone filler quality for each industry branch is defined by appropriate standards or requirements of manufacturers who use limestone as raw material in their production cycle. Limestone quality requirements are defined as content of useful and damaging components, i.e. as chemical composition, as well as the necessary size class. New production process scheme for processing limestone Glavatske Kuće in order to obtain fillers for the various branches of industry is shown in the Figure 6 i Figure 7.

3.1. EVALUATION OF "GLAVATSKE KUĆE" LIMESTONE FILLER QUALITY BASED ON CHEMICAL COMPOSITION

According to the results presented above, limestone from "Glavatske Kuće" – Kotor deposit can be used in the following industries:

- in the paint and coating industry; where, according to market requirements and standards, it belongs to the C, D and E quality classes, while for the highest quality A and B classes, this limestone is no satisfactory degree of whiteness (SRPS EN ISO 3262-5:2009);
- in foundry industry; it belongs to the highest class I in accordance with market requirements imposed by standard (SRPS B.B6.012);
- in sugar industry; it is among the II class (due to the increased MgO content) in accordance with market and standard requirements (SRPS B.B6.013);
- in metallurgy; it is in the highest class I in accordance with market requirements imposed by standards (SRPS B.B6.011);
- in production of glass; due to the increased Fe_2O_3 and MgO content it is in quality category IV and V in accordance with market requirements imposed by standards (SRPS B.B6.020);
- Limestone from "Glavatske Kuće" – Kotor deposit cannot be used:
- in the paper industry; because its degree of whiteness, among other things, is not satisfactory (SRPS B.B6.033);
- in pharmaceutical and cosmetics industry because its low whiteness degree and increased content of heavy metal Cd relative to market requirements defined by standard (SRPS B.B6.034);

- in the rubber and PVC industry; due to Cu content (47ppm) it does not meet market requirements and standards, which are strictly defined (SRPS B.B6.031),
- for production of mineral fertilizers because of the increased MgO content, which is strictly defined by manufacturer's requirements (Azotara Pančevo);
- in production of cattle feed because of the increased content of heavy metals Cu and Cd, which is very strictly defined for this use ("Official Gazette of the Republic of Serbia 2/90, 20/00, 4/2010; 54/2017);
- for neutralization of acidic soils; because of the increased content of MgO, P_2O_5, K_2O and Cu as biogenic elements and heavy metals Ni and Cd, the contents of which are very strictly defined ("Official Gazette of the Republic of Serbia" 60/00, 41/09, 84/2017).

3.2. EVALUATION OF "GLAVATSKE KUĆE" – KOTOR LIMESTONE FILLER QUALITY BASED ON USERS' REQUIREMENTS FOR THE NECESSARY RAW MATERIAL SIZE (FINENESS)

Some industries require finely micronized limestone, while others require raw material of larger particle size, sometimes even coarse. Following industries use ground and micronized limestone:

- for paints and coatings industry; A quality 99.5% of - 20µm, B quality 97% of -20µm and 0.01% of + 44µm;
- for glass industry, since "Glavatske Kuće" limestone corresponds to quality IV and V according to its chemical composition, there is predefined granulometric composition for these quality classes, subdivided into six subclasses in size range from -1+0.1mm;
- Following industries demand larger sizes and coarse limestone:
- for foundry industry, raw material should be size -50+30 mm, with class – 30 mm content up to 5%<;
- for sugar industry, limestone is to be classified into six subclasses in size range from -215+63mm, with maximum fine content in each subclass up to 8%;
- metallurgy uses limestone consisting of five subclasses in size range from -70+0.1mm.

4. THE TECHNOLOGICAL SCHEMES

Exploitation of raw materials would be done by drilling and blasting of which would be received blasted stone with GGK (upper size limit) of 450 mm. Below the primary bunker is stationary grid (pos. 3) 20 mm aperture, which serves to separate the waste rock in it (earth, clay and small stones faction), which is transported with conveyor belt on tailing

Raw-sized 32 mm from the plant for crushing and screening goes to grinding in order to obtain milled product which is used as filler in a variety of industries that require raw and micronized limestone which "Glavatske Kuće" matched its quality. Grinding is used as the starting sieved material or can optionally be sent to the grinding classified material from any stock from S8 to S12. The technological scheme of grinding and classification of limestone "Glavatske Kuće" is reperesented in Figure 7.

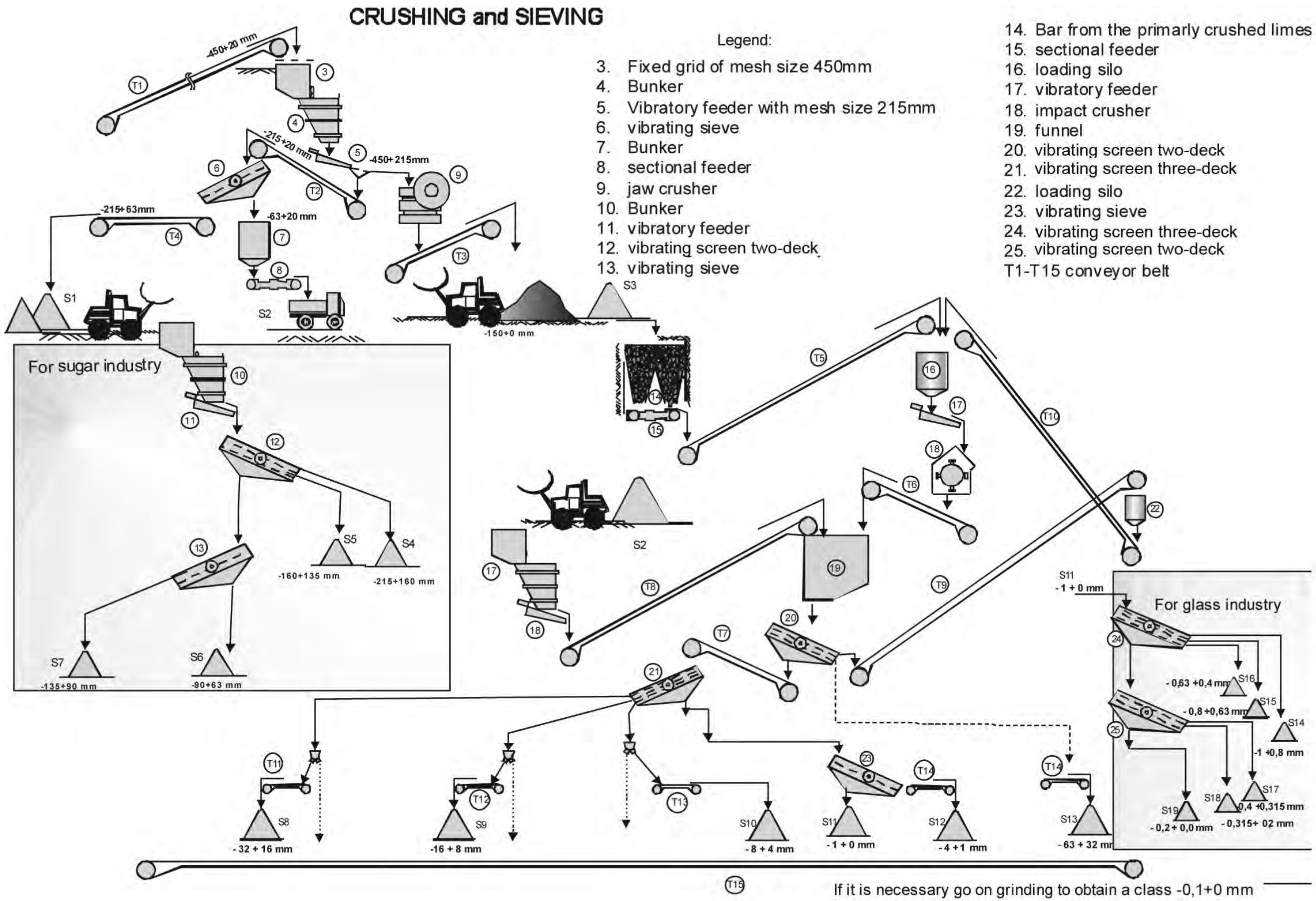

Figure 6. Technological scheme of crushing and sieving of limestone deposits "Glavatske Kuće" - Kotor

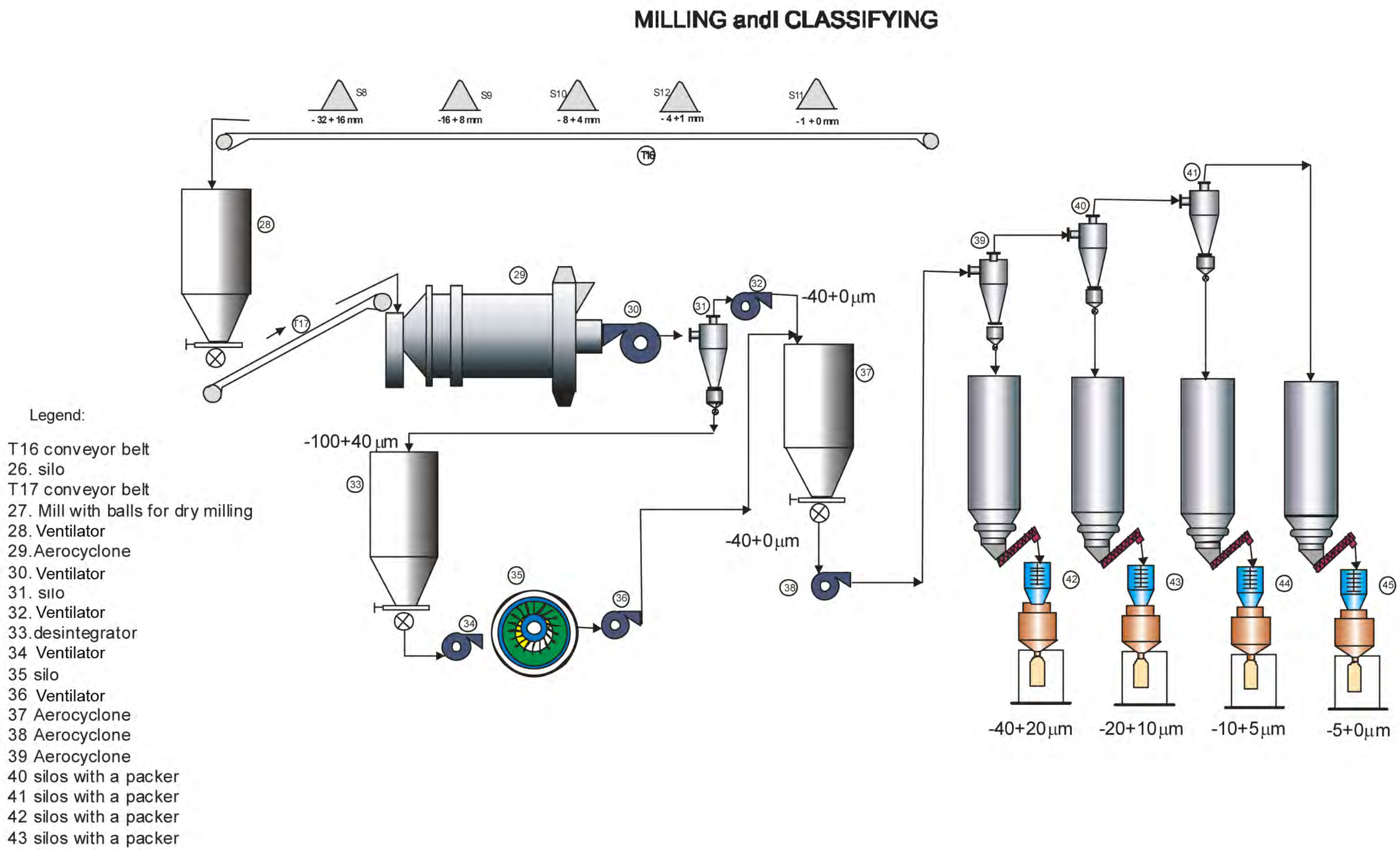

Figure 7. Technological scheme of grinding and classification of limestone deposit "Glavatske Kuće"-Kotor

5. CONCLUSION

Limestone from “Glavatske Kuće”- Kotor deposit according to its physico-chemical properties belongs to high quality carbonate raw material with high $CaCO_3$ content of 97.68 %, and low $MgCO_3$ content of 1.849 % and silicates (SiO_2 0.24 %). It meets the requirements of standards for using calcium carbonates as fillers in industry of paints and coatings; glass industry; foundry industry; sugar industry and metallurgy. According to market demand and standards it belongs to high quality raw material in the foundry industry and metallurgy. However, for the paint and coating industry; glass production, and sugar industry, this limestone does not belong to the highest quality classes defined by the standards, so it can be used as filler of lower quality in these industries.

Due to the low level of whiteness, “Glavatska kuća” limestone cannot be used in the paper, pharmaceutical and cosmetic industries. In addition, this limestone cannot be used in the pharmaceutical and cosmetic industries due to the increased content of heavy metals (Cd 8 ppm). Due to high content of heavy metals Cu (47 ppm) and Cd (8 ppm), limestone “Glavatske kuće” cannot be used in the production of cattle feed. Because of increased MgO content, limestone “Glavatske kuće” cannot be used in the fertilizers industry. Due to the high content of heavy metals Ni (50 ppm) and Cd (8 ppm), as well as biogenic elements MgO (0,884 %), Cu (47 ppm), P_2O_5 (0,0234 %), and K2O (0,0157 %), limestone “Glavatske kuće” cannot be used for neutralization of acidic soils.

By obtaining a wide range of fillers for different industrial branches (according to the technological scheme shown in Figures 6 and 7), products would be obtained that are up to 10 times more expensive per unit mass than the products that have been used so far.

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REZIME

Krečnjak je sedimentna stena koja pretežno sadrži karbonatne minerale (tj. kalcijum karbonat, $CaCO_3$) u količini koja prelazi 50%. Kvarc i minerali gline (npr. kaolinit, vodni liskun, montmorilonit) su druga dva glavna sastojka krečnjaka Budući da je najzastupljeniji i obuhvata najmanje 50% svih prisutnih mineralnih faza u krečnjaku, kalcit je važan resurs i predmet istraživanja u različitim naučnim oblastima: mineralogiji, hemiji, fizici, nauci o materijalima.

Kalcit ($CaCO_3$) je jedan od najčešćih minerala na Zemlji, koji čini oko 4% mase Zemljine kore. Kalcit se javlja u karbonatima i nefelinskim sijenitima kao primarna komponenta magmatske faze, a čest je i u hidrotermalnim naslagama. U metamorfoziranim naslagama, kalcit se javlja u obliku mermera. U karbonatima, dolomit (Ca, Mg)CO_3, magnezit ($MgCO_3$), siderit ($FeCO_3$), rodohrozit ($MnCO_3$) i smitsonit ($ZnCO_3$) se javljaju kao izomorfni sa kalcitom.

Kalcit se koristi za proizvodnju kreča i portland cementa, dok se u građevinarstvu primenjuje kao lomljeni ili ukrasni kamen. Kalcijum je takođe važan mikronutrijent. Nekoliko komercijalnih lekova (antacidi i suplementi kalcijuma) su, u stvari, mleveni krečnjak. Značajna je i njegova primena kao punila, u raznim granama industrije (farmaceutska, stočna, PVC i gumarska, industrija boja i lepkova, industrija mineralnih đubriva, livnica, metalurgija, itd.), kao i u poljoprivredi gde se koristi za podešavanje pH vrednosti zemljišta.

Republika Crna Gora ima velike rezerve krečnjaka u primorju i na jugu teritorije. Iako su nalazišta ogromna, krečnjak se uglavnom koristi u građevinarstvu kao građevinski kamen, a donekle i kao arhitektonski kamen.

S obzirom da je kalcijum karbonat kao punilo mnogo skuplji od građevinskog kamena, nadležne institucije Crne Gore su pokrenule ispitivanje mogućnosti upotrebe krečnjaka kao punila. Ležište “Glavatske Kuće”-Kotor sastoji se od karbonatnih sedimenata, uglavnom krečnjačkih, a manje dolomitskih sedimenata.
Rezerve rude se procenjuju na oko 15.000.000 t krečnjaka. Cilj istraživanja predstavljenih u ovom radu bio je da se utvrdi mogućnost upotrebe sirovine kao punila u različitim industrijskim granama.

Početni uzorak krečnjaka korišćen u istraživanjima bio je sa „Glavatske kuće” - ležište Kotor. Prvo je određena njegova specifična zapreminska težina (gustina) i granulometrijski sastav. Gustina mu je merena piknometrom sa ksilolom kao tečnim, granulometrijski sastav je određen Tiler screenom. Granulometrijski sastav mikronizovanog uzorka određen je sitom veličine 63 µm, klasifikacijom na Ciclosizeru i Bach elutriatoru.

Kvalitet krečnjačkog punila određen je hemijskom, mineraloškom (KSRD), DT/TG i FTIR spektroskopskom analizom.
Stepen beline je određen meračem beline, prema MgO 100% standardu. Mineraloška analiza uzoraka krečnjaka obavljena je tehnikom rendgenske difrakcije praha (KSRD).

Obrasci difrakcije rendgenskih zraka na prahu su dobijeni na automatizovanom difraktometru Philips PV-1710 korišćenjem Cu cevi koja radi na 40 kV i 30 mA. Termičko ponašanje je praćeno simultanom diferencijalnom termičkom analizom (DTA) i termogravimetrijom (TG) u temperaturnom opsegu od 20^o C do 1000^o C. DTA/TG analize su prenošene u statičkom protoku vazduha automatskom termo-analizom. sistem: STA 409EP (Netzsch, Nemačka).

Hemijske veze, karakteristični molekularni otisci prstiju, funkcionalne grupe i informacije o kovalentnom vezivanju otkrivene su analizom Fourier Transform Infracrvene (FTIR) spektroskopije.

FTIR spektri su dobijeni na Nicolet IS-50 spektrometru (Thermo Fisher Scientific, SAD), snimljenom u KBr transmisionom režimu u opsegu 4000-400 cm-1 i 32 skeniranja pri rezoluciji 4.

Morfologija uzoraka je okarakterisana skenirajućim elektronskim mikroskopom (JEOL JSM–6610LV). Ispitivani uzorci su prekriveni zlatom korišćenjem mašine za raspršivanje tipa BALTEC-SCD-005 radi poboljšanja provodljivosti pre snimanja.

Tehnološka šema za proizvodnju punila na bazi krečnjaka "glavatske kuće"-kotor Krečnjak sa ležišta „Glavatske kuće" – Kotor, zbog svojih fizičko-mehaničkih svojstava može se koristiti u različite svrhe kao tehničko-građevinski kamen, a po svom hemijskom sastavu može se koristiti kao sirovina za punila za različite industrije. Zbog toga je neophodno da tehnološka šema pripreme krečnjaka „Glavatske kuće" u sledećim operacijama sadrži prečistače koji bi dobijali različite veličine proizvoda za široku primenu u mnogim industrijama.

Tehnološka šema je projektovana na veoma fleksibilan način, tako da se, u zavisnosti od potreba potrošača i prerađivačkih kapaciteta, proizvodnja odvija na način da se svaka veličina klase dobija u više smena, a zatim u skladu sa zahtevima tržišta, premošćavanjem pozicija tehnologije i povezivanja dobijaju druge proizvode različite klase veličine. Tehnološka šema drobljenja i prosejavanja prikazana je na slici 6.

Krečnjak sa ležišta "Glavatske Kuće" – Kotor po svojim fizičko-hemijskim svojstvima pripada visokokvalitetnoj karbonatnoj sirovini sa visokim sadržajem $CaCO_3$ od 97,68 % i niskim sadržajem $MgCO_3$ od 1,849 % i silikata (SiO_2 0,24 %).

Ispunjava zahteve standarda za upotrebu kalcijum karbonata kao punila u industriji boja i premaza; industrija stakla; livnička industrija; industrije šećera i metalurgije. Po potražnji i standardima tržišta spada u visokokvalitetne sirovine u livačkoj industriji i metalurgiji. Međutim, za industriju boja i premaza; u proizvodnji stakla, industriji šećera, ovaj krečnjak ne pripada najvišim klasama kvaliteta definisanim standardima, pa se u ovim industrijama može koristiti kao punilo nižeg kvaliteta.

Zbog niskog stepena beline, krečnjak „Glavatska kuća" ne može se koristiti u papirnoj, farmaceutskoj i kozmetičkoj industriji. Osim toga, ovaj krečnjak se ne može koristiti u farmaceutskoj i kozmetičkoj industriji zbog povećanog sadržaja teških metala (Cd 8 ppm). Zbog visokog sadržaja teških metala Cu (47 ppm) i Cd (8 ppm), krečnjak „Glavatske kuće" ne može se koristiti u proizvodnji stočne hrane. Zbog povećanog sadržaja MgO, krečnjak „Glavatske kuće" ne može se koristiti u industriji đubriva. Zbog visokog sadržaja teških metala Ni (50 ppm) i Cd (8 ppm), kao i biogenih elemenata MgO (0,884 %), Cu (47 ppm), P2O5 (0,0234 %) i K2O (0, 0157 %), krečnjak „Glavatske kuće" se ne može koristiti za neutralizaciju kiselih zemljišta.

Dobijanjem širokog spektra punila za različite industrijske grane (prema tehnološkoj šemi prikazanoj na slikama 6 i 7) dobijali bi se proizvodi koji su i do 10 puta skuplji po jedinici mase od proizvoda koji su do sada korišćeni.

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