UNIVERSITY OF BELGRADE
TECHNICAL FACULTY IN BOR
CHAMBER OF COMMERCE AND
INDUSTRY OF SERBIA

PROCEEDINGS

XIII International MINERAL PROCESSING and RECYCLING CONFERENCE

Editors:
Grozdanka Bogdanović
Milan Trumić

Belgrade, Serbia, 8 – 10 May 2019

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OBTAINING FILLERS BASED ON LIMESTONE FROM DEPOSIT "BRIJEG"-ULCINJ FOR APPLICATIONS IN VARIOUS INDUSTRIES

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ABSTRACT – Paper presents results of investigations of the possibility of using "Brijeg"-Ulcinj limestone as filler in various industries. Micronization, granulometric composition, oil and water absorption and degree of whiteness were investigated, and chemical and thermal analyses were performed.
Physico-chemical properties of this sample classify it among high quality carbonate raw materials with high $CaCO_3$ content of 98.21%, with low contents of $MgCO_3$ 0.88 % and SiO_2 0.16 %. Its quality satisfies requirements of standards on using of calcium carbonate as filler in next industries: paints and coatings; rubber and PVC; glass; foundry ; sugar industry production of mineral fertilizers and metallurgy.

Key words: limestone, filler, industrial use, standards.

INTRODUCTION

Republic of Montenegro has big reserves of limestone in coastal area and in south of the territory [1]. Even though deposits are huge, limestone is mainly used in construction as construction stone, and to some extent as architectural stone [2]. 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 [3]. 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 [4-6].

"Brijeg"-Ulcinj deposit consists of carbonate sediments, mostly limestone ones, and less dolomitic sediments. Ore reserves are estimated at about 3,000,000 t of limestone [1]. The aim of investigations presented in this paper was to determine the

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possibility of using raw material as filler in various industry branches.

EXPERIMENTAL

Materials and methods

Starting limestone sample used in investigations was from "Brijeg" - Ulcinj deposit. First, its specific volumetric weight (density) was measured by pycnometer, and granulometric composition were determined by Tyler screen [7]. 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 analysis. Thermal (DT/TG) analysis of the sample was performed using Netzsch-Simultaneous Thermal Analysis- STA 409 EP device, with heating speed of ΔT = 10 °C /min, in temperature interval from 20 to 1000 °C. Degree of whiteness was determined by whiteness meter, according to MgO 100 % standard.

Investigation of physical properties of starting sample

Specific volumetric weight of the starting sample is γ= 2.712 g / cm^3. Based on data from the table 1 is drown a diagram of particle size distribution shown in Figure 1, for samples of limestone Brijeg. In Figure 1, shows the direct curve of particle size distribution and cumulative curves and average sample of outflow and flow limestone deposits "Brijeg"-Ulcinj. From the intersection of cumulative curves average outflow and flow determined that the average diameter of the sample of limestone d_{50}=4.93 mm, and upper size limit of the sample was 14.76 mm.

Table 1. Granulometric-composition of the initial sample Brijeg- Ulcinj

Size class [mm]	M, %	↓∑ M, %	↑∑ M, %
- 19.1 + 15.9	2.66	2.66	100.00
- 15.9 + 12.7	8.58	11.24	97.34
- 12.7 + 9.52	17.22	28.46	88.76
- 9.52 + 7.93	8.06	36.52	71.54
- 7.93 + 5.0	12.89	49.41	63.48
- 5.0 + 3.36	16.28	65.69	50.59
- 3.36+ 2.38	5.13	70.82	34.31
- 2.38+ 1.6	6.74	77.56	29.18
- 1.6+ 1.19	5.08	82.64	22.44
- 1.19+ 0.63	6.96	89.60	17.36
- 0.63 + 0.4	3.03	92.63	10.40
- 0.400 + 0.300	1.57	94.20	7.37
- 0.300 + 0.200	1.51	95.71	5.80
- 0.200 + 0.000	4.29	100.00	4.29
Input	100.00	/	/

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, thermal

(DT/TG) analysis, determination of granulometric composition, degree of whiteness and absorption of oil and water.

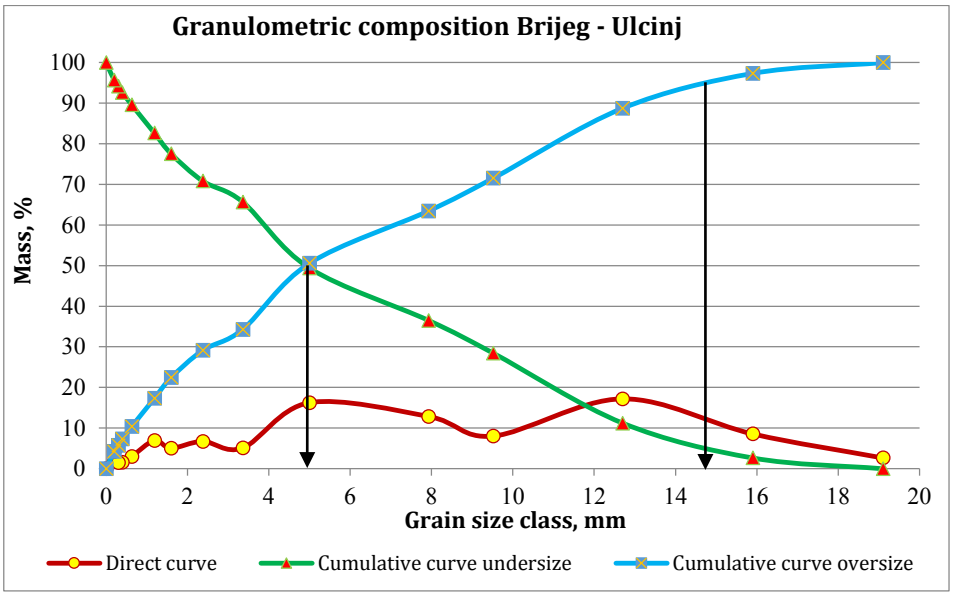

Figure 1. The curves of particle size-composition of the starting sample "Brijeg"-Ulcinj

Determining granulometric composition of micronized sample

Granulometric composition of the micronized products is represented in Table 2, and showed that upper size limit is 85 μm, and that the finest class - 5.7 μm content is around 11 %.

Table 2. Granulometric composition of grinded sample Brijeg

Size class [μm]	M, %	↓∑ M, %	↑∑ M, %
+ 63	33.32	33.32	100.00
-63+44	5.27	38.59	66.68
-44+33	7.13	45.72	61.41
-33+23	5.80	51.52	54.28
-23+15	4.07	55.59	48.48
-15+11	3.87	59.46	44.41
-11+5.7	29.4	88.86	40.54
-5.7+0	11.14	100.00	11.14
Input	100.00	/	/

Determining the degree of whiteness

Whiteness was assessed on three samples of the limestone from deposit "Brijeg", and the result is shown in Table 3.

Table 3. The degree of whiteness the limestone samples

No	mark of the sample	whiteness according MgO - 100 %
1.	Brijeg-1	85.90
2	Brijeg-2	84.80
3	Brijeg-3	85.80
	Average value	85.50

Determination of absorption water and oil

In order to determine absorption water and oil are also used three samples of the limestone from deposit "Brijeg", and the results are shown in Tables 4 and 5.

Table 4. Absorption of the oil of samples of limestone

No.	mark of the sample	absorption of the oil, %
1.	Brijeg-1	13.42
2.	Brijeg-2	13.65
3.	Brijeg-3	13.52
	Average value	13.53

Table 5. Absorption of the water of samples of limestone

No.	mark of the sample	absorption of the water, %
1.	Brijeg-1	18.51
2.	Brijeg-2	18.77
3.	Brijeg-3	18.67
	Average value	18.65

Thermal (DT/TG) analysis

Results of thermal (DTA/TG) analysis of the micronized sample “Brijeg” limestone are presented as a diagram in Figure 2.

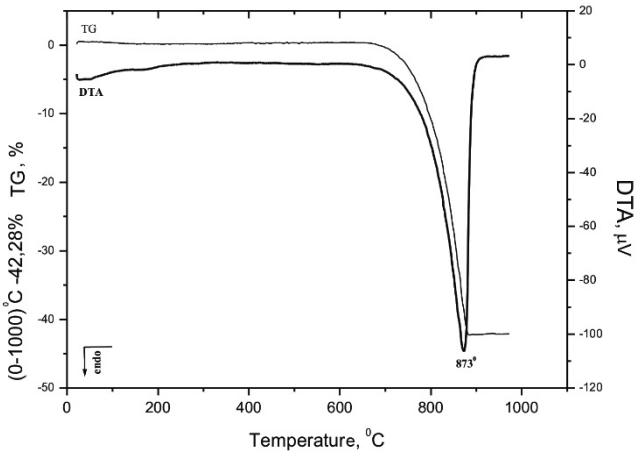

Figure 2. DTA/TG diagram of ”Brijeg” limestone sample

In Figure 2 are presents the TG and DTA diagrams of the initial sample of limestone. DTA diagram (Figure 2.) shows endothermic peak with maximum at 873 °C, which is attributed to phase transformation of calcite ($CaCO_3$) into CaO, according to the following reaction:

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

This phase transformation is accompanied by weight loss of 42.28 % (TG diagram, Figure 2) in the temperature range from 650 °C to 900 °C.

Chemical analysis

Results of chemical analysis of the micronized limestone with contents of main components and damaging components are presented in Tables 6 and 7.

Table 6. Chemical composition of main components of limestone sample

Component	Cont., %
CaO	55.03
$CaCO_3$	98.21
CO_2	43.19
MgO	0.88
Fe_2O_3	0.028
Al_2O_3	0.022
R_2O_3	0.048
SiO_2	0.16
K_2O	0.0052
Na_2O	0.025
TiO_2	< 0.02
P_2O_5	< 0.005
LOI	43.62

Table 7. Chemical composition of damaging components of limestone sample

Component	Cont., %
Cu	9
Mn	27
S	< 0.01
P	< 25
Ni	21
Cr	6
Mo	< 50
Pb	25
Cd	4
pH	9.28
Fe solu.	200
As	/
Hg	/

Results of physico-chemical characterization of "Brijeg" 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 - 98.21 %, and $MgCO_3$ (1.84 %) and silicates (SiO_2 0.16 %) content low. However, relatively high content of heavy metals was found, above all Cu (9 ppm), Pb (25 ppm), Ni (21 ppm) and Cd (4 ppm).

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.

Evaluation of "Brijeg" limestone filler quality based on chemical composition

According to the results presented above, limestone from "Brijeg" – Ulcinj deposit can be used in the following industries:

- in industry of paints and coatings; it is among high quality raw materials in accordance with market and standard requirements (SRPS B.B6.032);
- in paper industry; it is among A, B quality, while for the C and highest D quality its whiteness degree is not satisfying (SRPS B.B6.033);
- in rubber and PVC industry; it satisfies the highest quality standards and market requirements (SRPS B.B6.031);
- 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; due to the increased MgO content it is in quality class II 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 MgO content it is in quality category IV and V in accordance with market requirements imposed by standards (SRPS B.B6.020);
- in production of phosphate mineral nutrients, in accordance with market requirements strictly defined for use ("Official Gazette of the Republic of Serbia" 31/78, 6/81, 2/90, 20/00).

Limestone from "Brijeg" – Ulcinj deposit cannot be used:

- 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);
- 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 Pb and Cd, which is very strictly defined for this use ("Official Gazette of the Republic of Serbia" 31/78, 6/81, 2/90, 20/00);
- for neutralization of acidic soils; because of the increased content of MgO, P2O5 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" 60/2000).

Evaluation of "Brijeg" – Ulcinj 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 + 44 μm;
- for paper industry for all quality categories (A, B and C) the required fineness is 100 % of - 45 μm, where for A quality 75 % of -10 μm, for B quality 80 %, and for C quality the required fineness is 95 % of -10 μm and 90 % of - 2 μm; rubber and PVC industry requires for A and B quality raw material to be 99.5 % of - 45 μm, while for C and D quality upper limit limestone size is 45 μm;
- for glass industry, since "Brijeg" 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 + 0.1 mm;

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 + 63 mm, with maximum fine content in each subclass up to 8 %;
- metallurgy uses limestone consisting of five subclasses in size range from - 70 + 0.1 mm.

CONCLUSION

Limestone from "Brijeg"- Ulcinj deposit according to its physico-chemical properties belongs to high quality carbonate raw material with high content of $CaCO_3$ of 98.21 %, and low content of $MgCO_3$ of 0.88 % and silicates (SiO_2 0.16 %). It meets the requirements of standards for using calcium carbonates as fillers in industry of paints and coatings; paper industry, rubber and PVC industry; foundry industry; sugar industry and metallurgy. According to market demand and standards it belongs to high quality raw material in industry of paints and coatings, rubber and PVC, foundry industry and metallurgy. However, for the sugar industry and the production of glass, it does not comfor with the highest standards.

Because of increased MgO content "Brijeg" limestone cannot be used in fertilizers industry. Due to high content of heavy metals Pb (25 ppm), Ni (21 ppm) and Cd (4 ppm), as well as biogenic elements MgO (0,88 %) and Cu (9 ppm), "Brijeg" limestone cannot be used in pharmaceutical and cosmetics industry, in production of cattle feed and for neutralization of acidic soils. Obtaining of wide range of fillers for various industry branches would provide products which are more expensive per mass unit than products that have been used until now up to 10 times.

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