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Ecological Truth

Editors
Radoje V. Pantovic
Zoran S. Marković

EcoIst '15

Hotel "PUTNIK", Kopaonik, SERBIA
17-20 June 2015

UNIVERSITY OF BELGRADE
TECHNICAL FACULTY BOR

XXIII International Conference

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OBTAINING FILLERS BASED ON LIMESTONE FROM DEPOSIT "RISTOVA PONTA" – ULCINJ, FOR APPLICATIONS IN VARIOUS INDUSTRIES

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ABSTRACT

Paper presents results of investigations of using limestone as filler. Micronization methods, granulometric composition, oil and water absorption and degree of whiteness were investigated, and chemical and thermal analyses were performed.

Physico-chemical properties classified, by quality, this limestone for use as filler in the following industries: paints and coatings; rubber and plastic; glass; foundry; sugar, metallurgy and paper production. Due to low degree of whiteness and high content of MgO, heavy metals, and biogenic elements this limestone cannot be used in folowing industries: pharmaceutical and cosmetics, in fertilizers, in production of cattle feed and for neutralization of acidic soils.

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 [3-6].

"Ristova Ponta"-Ulcinj deposit consists of carbonate sediments, mostly limestone ones, and less dolomitic sediments. Ore reserves are estimated at about 2,500,000 t of limestone [1]. The aim of investigations presented in this paper was to determine the possibility of using raw material as filler in various industry branches.

EXPERIMENTAL

Materials and methods

Starting limestone sample used in investigations was from "Ristova Ponta" - Ulcinj 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 [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 $\Delta T = 10\ ^0C/min$, in temperature interval from 20 to 1000 ^0C. 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 $\gamma = 2{,}679\ g/cm^3$.

Table 1. Granulometric-composition of the initial sample Ristova Ponta- Ulcinj

Size class, [mm]	M, %	↓∑M, %	↑∑ M, %
+ 22,2	/	/	
-22,2 + 19,1	/	/	
- 19,1 + 15,9	3,68	3,68	100,00
- 15,9 + 12,7	9,48	13,16	96,32
- 12,7 + 9,52	17,23	30,39	86,84
- 9,52 + 7,93	7,88	38,27	69,61
- 7,93 + 5,0	13,83	52,10	61,73
- 5,0 + 3,36	14,99	67,09	47,90
- 3,36+ 2,38	4,74	71,83	32,91
- 2,38+ 1,6	5,98	77,81	28,17
- 1,6+ 1,19	4,91	82,72	22,19
- 1,19+ 0,63	6,63	89,35	17,28
- 0,63 + 0,4	2,93	92,28	10,65
- 0,4 + 0,3	1,69	93,97	7,72
- 0,300 + 0,200	1,62	95,59	6,03
- 0,200 + 0,000	4,41	100,00	4,41
Input	100,00	/	/

Based on data from the table is drown a diagram of particle size distribution shown in Figure 1, for samples of limestone Ristova Ponta. In Figure 1, shows the direct curve of particle size distribution and cumulative curves and average sample of outflow and flow limestone deposits "Ristova Ponta"-Ulcinj. From the intersection of cumulative curves average outflow and flow determined that the average diameter of the sample of limestone $d_{50} = 5.42$ mm, and upper size limit of the sample was 15.32 mm**.**

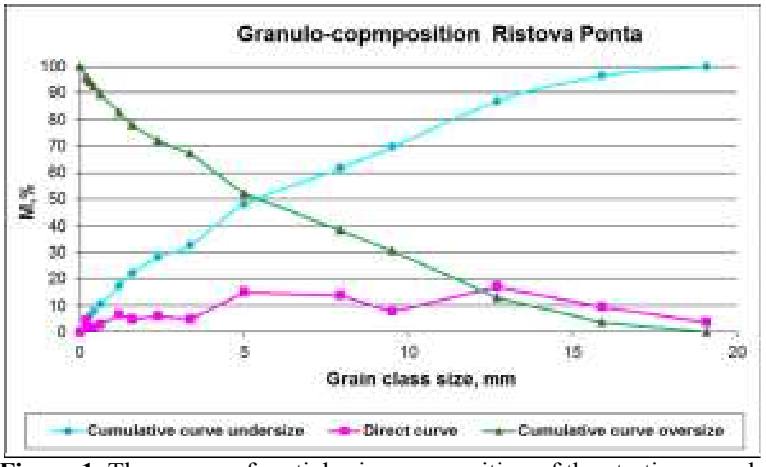

Figure 1. The curves of particle size-composition of the starting sample "Ristova Ponta"-Ulcinj

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.

Determining granulometric composition of micronized sample

Table 2. Granulometric composition of grinded sample Ristova Ponta

Size class [μm]	M, %	↓∑M, %	↑∑ M, %
+ 63	25,33	25,33	100,00
-63+44	4,48	29,81	74,67
-44+33	7,02	36,83	70,19
-33+23	5,08	41,91	63,17
-23+15	3,66	45,57	58,09
-15+11	3,66	49,23	54,43
-11+5,7	35,54	84,77	50,77
-5,7+0	15,23	100,00	15,23
Input	100,00	/	/

Granulometric composition of the micronized products showed that upper size limit is about 90 μm, and that the finest class -5.7 μm content is around 15 %.

Determining the degree of whiteness

Whiteness was assessed on three samples of the limestone from deposit "Ristova Ponta", 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.	Ristova Ponta-1	86.30
2	Ristova Ponta-2	85.60
3	Ristova Ponta-3	86.10
	Average value	86.00

Determination of absorption water and oil

In order to determine absorption water and oil are also used three samples of the limestone from deposit "Ristova Ponta", 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.	Ristova Ponta-1	13,92
2.	Ristova Ponta-2	14,05
3.	Ristova Ponta-3	14,06
	Average value	14,01

Table 5. Absorption of the water of samples of limestone

No	mark of the sample	absorption of the water, %
1.	Ristova Ponta-1	19,01
2.	Ristova Ponta-2	19,17
3.	Ristova Ponta-3	19,13
	Average value	19,1

Thermal (DT/TG) analysis

Results of thermal (DTA/TG) analysis of the micronized sample "Ristova Ponta" limestone are presented as a diagram in Figure 2.

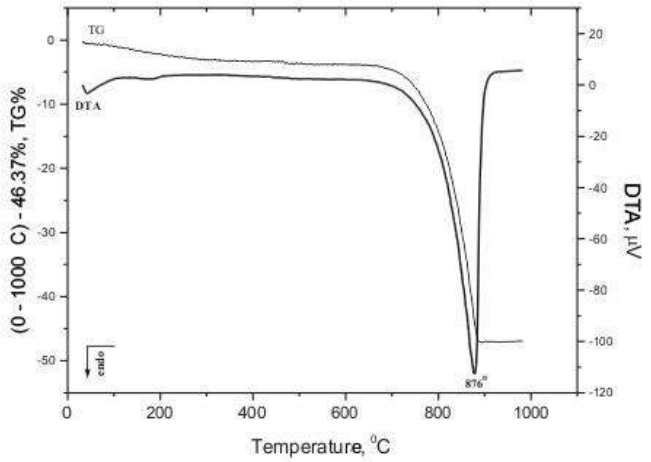

Figure 2. DTA/TG diagram of "Ristova Ponta" limestone sample

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 876 ^{0}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 46.37% (TG diagram, Figure 2) in the temperature range from 650 ^{0}C to 900 ^{0}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

Comp.	CaO	$CaCO_3$	CO_2	MgO	Fe_2O_3	Al_2O_3	R_2O_3
Cont., %	54,75	97,72	43,50	1,04	0,0388	0,021	0,0258
Comp.	SiO_2	K_2O	Na_2O	TiO_2	P_2O_5	LOI	
Cont., %	0,064	0,0066	0,0244	<0,02	<0,005	43,63	

Table 7. Chemical composition of damaging components of limestone sample

Comp.	Cu	Mn	S	P	Ni	Cr	Mo
Cont., %	8ppm	35ppm	<0,01	<0,0025	19ppm	4 ppm	<50 ppm
Comp.	Sb	Pb	Cd	pH	Fe solu.	As	Hg
Cont., %	<25 ppm	25 ppm	2ppm	9,07	0,0340	/	/

Results of physico-chemical characterization of "Ristova Ponta" 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- 97.72%, and $MgCO_3$ (2,18%) and silicates (SiO_2 0.064%) content low. However, relatively high content of heavy metals was found, above all Cu (8 ppm), Mn (35 ppm), Ni (19 ppm) and Cd (2 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 "Ristova Ponta" limestone filler quality based on chemical composition

According to the results presented above, limestone from "Ristova Ponta" – 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 rubber and PVC industry; it satisfies the highest quality standards and market requirements (SRPS B.B6.031);
- in paper industry, because its relatively low whiteness degree it satisfies A, B and C quality class in accordance with market and standard requirements (SRPS B.B6.033)
- 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);

Limestone from "Ristova Ponta" – Ulcinj deposit cannot be used:

- in pharmaceutical and cosmetics industry because its low whiteness degree 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, and K_2O as biogenic element and heavy metals, Cu, Pb, Ni and Cd, the contents of which are very strictly defined ("Official Gazette of the Republic of Serbia" 60/2000).

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

CONCLUSION

Limestone from "Ristova Ponta"- Ulcinj deposit according to its physico-chemical properties belongs to high quality carbonate raw material with high content of $CaCO_3$ of 97.72%, and low content of $MgCO_3$ of 2.18% and silicates (SiO_2 0.064%). It meets the requirements of standards for using calcium carbonates as fillers in industry of paints and coatings; paper industry, glass 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 sugar industry and glass production it does not conform to standards. Because of increased MgO content "Ristova Ponta" limestone cannot be used in fertilizers industry. Due to low whiteness degree (86,0%) limestone "Ristova Ponta"cannot be used in in pharmaceutical and cosmetics industry. Due to high content of MgO, heavy metals Ni (19 ppm) Pb (25ppm) and Cd (2 ppm), as well as biogenic elements Cu (8 ppm) and K_2O (0.0066%), "Ristova Ponta" limestone cannot be used 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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REFERENCES

1. Izveštaj o ispitivanju krečnjaka sa područja Crne Gore, za primenu kao punioca u različitim granama industrije, Arhiva ITNMS, Beograd, 2011.
2. http://geology.com/usgs/limestone/
3. Slavica Mihajlović:"Fizičko-hemijsko modifikovanje kalcita stearinskom kiselinom, doktorska disertacija, Rudarsko-geološki fakultet Beograd, 2011.
4. Živko T. Sekulić: "Kalcijum karbonatne i kvarcne sirovine i njihova primena", Monografija, ISBN 978-86-82867-24-1, ITNMS, Beograd, 2011., str. 21-75.
5. www.patentgenius.com/patent/4026762"Use of ground limestone as a filler in paper"
6. http://minerals.usgs.gov/minerals/pubs/commodity/stone_crushed/mcs-2010-stonc.pdf
7. Radica Milosavljević:"Metode ispitivanja mineralnih sirovina u pripremi mineralnih sirovina", Rudarsko-geološki fakultet Beograd, 1974.