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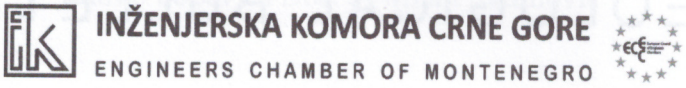

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SADRŽAJ – CONTENTS

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LIMESTONE FROM DEPOSIT "MALJAT"-DANILOVGRAD-POTENTIAL RAW MATERIAL FOR OBTAING FILLERS

Abstract

The possibility of using limestone "Maljat"-Danilovgrad as filler was investigated. Micronization, granulo-composition, oil and water absorption and degree of whiteness were investigated, and chemical and thermal analyses (DT/TG) were performed. Physical-chemical properties of this limestone classify it among high quality carbonate raw materials. It can be used in following industry: paints and coatings; paper; rubber and PVC; glass; production of mineral fertilizers; foundring; sugar, metallurgy and in production of cattle feed. Due to content of P_2O_5, cannot be used for neutralization of acidic soils.

Key words: limestone-Maljat, filler, industrial use, standards

KREČNJAK IZ LEŽIŠTA "MALJAT"-DANILOVGRAD-POTENCIJALNA SIROVINA ZA DOBIJANJE PUNIOCA

Abstrakt

U radu je ispitivana mogućnost korišćenja krečnjaka "Maljat"-Danilovgrad kao punioca. Ispitivana je mikronizacija, granulo-sastav, upijanje vode i ulja i stepen beline, urađena je hemijska i termijska (DT/TG) analiza. Fizičko-hemijske osobine svrstavaju ovaj krečnjak u veoma kvalitetne karbonatne sirovine. On može biti korišten u sledećim industrijama: boja i premaza, papira, gume i PVC-a, stakla, proizvodnji mineralnih djubriva, livarstvu, šećera, metalurgiji i proizvodnji stočne hrane. Zbog sadržaja P_2O_5 ne može se koristiti za neutralizaciju kiselih zemljišta.

Ključne reči: krečnjak-Maljat, punioc, industrijska upotreba, standardi

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1. 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 [3-11].

"Maljat"-Danilovgrad deposit consists of carbonate sediments, mostly limestone ones, and less dolomitic sediments. Out of total reserves of 4,000,000 t of limestone, only 23% is used for production of commercial blocks [1]. Due to its quality, according to standard (SRPS B.B3. 200), stone from "Maljat" deposit is used as architectural-construction stone for internal and external cladding. The aim of investigations presented in this paper was to determine the possibility of using the rest of raw material (77%) as filler in various industry branches.

2.0 EXPERIMENTAL

To investigate the potential use of limestone as filler, a sample was prepared and analyzed by standard methods of preparation of mineral resources. In the primary sample was determined by grain size distribution, moisture and rough-specific density [12-15]. All three samples of limestone "Maljat", in which rough moisture was assessed, were been dry. After that, a starting sample is micronised, and on it has been carried out technological tests.

2.1 MATERIALS AND METHODS

Starting limestone sample used in investigations was from "Maljat" - Danilovgrad 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 [12]. Micronization of limestone were carried out in a vibrating mill with ring working elements, model "MN 954/3" (manufacturer "KHD Humboldt Wedag"— Germany). 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.

2.2 INVESTIGATION OF PHYSICAL PROPERTIES OF STARTING SAMPLE

2.2.1 Specific volumetric mass

The specific density (density) of the sample of limestone "Maljat" was determined on three samples and data that is shown is actually the mean density of the sample of limestone "Maljat". All measured values are rounded to the third decimal value.

$$\gamma = 2{,}681 \text{ g/cm}^3$$

2.2.2 Granulometric composition of the initial sample of limestone

Granulometric composition of the starting sample was determined to standard sieving methods on to Tyler's series of sieves [12-15]. Based on obtained data from sieving is drawn a diagram of particle size distribution shown in Figure 1, for samples of limestone Maljat.

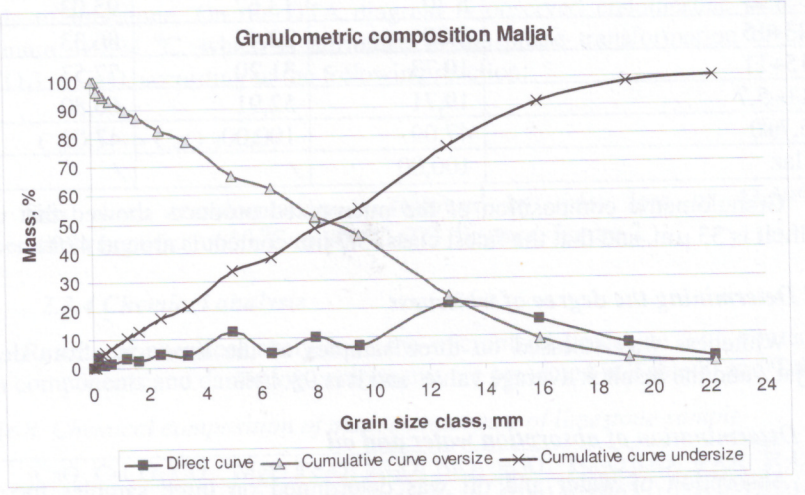

Figure 1 The curves of particle size-composition of the starting sample of limestone "Maljat"-Danilovgrad

In Figure 1, shows the direct curve of particle size distribution and cumulative curves and average sample of outflow and flow limestone deposits "Maljat"-Danilovgrad. From the diagram (Figure 1) can be seen that the upper size limit of initial sample was 18,5 mm, and the average diameter of the sample of limestone was d_{50} = 8.49 mm.

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

2.3.1 Granulometric composition of micronized product

The total balance of granulometric composition of the micronized sample-limestone "Maljat" is shown in Table 1.

Table 1. Granulometric composition of grinded sample Maljat

Grain size class [μm]	M, %	↓ΣM, %	↑Σ M, %
-63+44	1.00	1,00	100,00
-44+33	3.97	4,97	99,00
-33+23	8.70	13,67	95,03
-23+15	8.80	22,47	86,33
-15+11	10.73	31,20	77,53
-11+5,7	19,71	52,91	66,80
-5,7+0	47,09	100,00	47,09
Ulaz	100,00	/	/

Granulometric composition of the micronized products showed that upper size limit is 33 μm, and that the finest class -5.7 μm content is around 47%.

2.3.2 Determining the degree of whiteness

Whiteness was assessed on three samples of the limestone from deposit "Maljat", and the result is average value, and it is 93.40%.

2.3.3 Determination of absorption water and oil

Absorption of water and oil was determined on three samples too. The presented results represent the average values of oil absorption of 13%, and water absorption of 19.20%.

2.3.4 Thermal (DT/TG) analysis

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

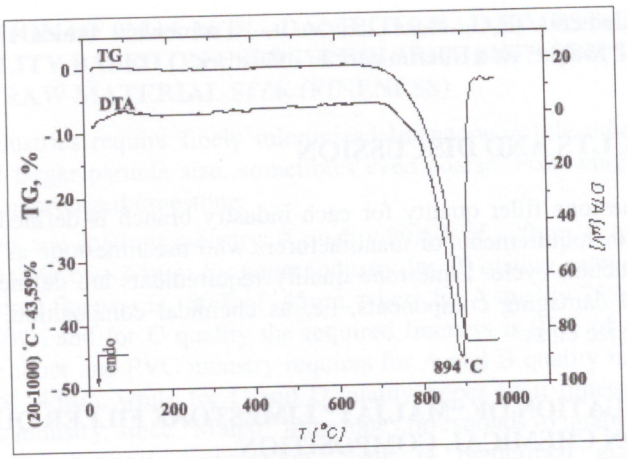

Figure 2. DTA/TG diagram of "Maljat" limestone sample

In Figure 2 were presented the curves of TG/DTA diagrams of the initial sample of limestone. On the DTA diagram is observed endothermic peak with maximum at 894 ^{0}C, which is attributed to the phase transformation of calcite ($CaCO_3$) in CaO, according to the following reaction:

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

This phase transformation is followed by mass loss of 43.59% in temperature range from 650 ^{0}C to 900^{0}C (TG diagram, Figure 2.).

2.3.4 Chemical analysis

Results of chemical analysis of the micronized limestone with contents of main components and damaging components are presented in Table 8. and Table 9.

Table 8. Chemical composition of main components of limestone sample

Comp.	CaO	$CaCO_3$	CO_2	MgO	Fe_2O_3	Al_2O_3	SiO_2	K_2O	Na_2O	TiO_2	P_2O_5	R_2O_3	LOI
Conte., %	55,56	99,22	43,81	0,260	0,043	0,0047	0,16	0,0014	0,046	<0,02	0,0312	0,048	43,85

Table 9. Chemical composition of damaging components of limestone sample

Comp.	Cu	Mn	Ni	Cr	Mo	Sb	Pb	Cd	As	Hg	pH	Fe rast.	S	P
	ppm											%		
Conte.	>5	16,5	>2	>10	>10	>10	>10	>0,5	-	-	9,40	0,016	<0,01	0,014

Results of physical-chemical characterization of "Maljat" 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- 99.22%, and $MgCO_3$ (0.55%) and silicates (SiO_2 0.16%) content low. However, relatively high content of

bogenic elements (P_2O_5 -0,0312%) in it, is somewhat limitation factor for use limestone-"Maljat" as a filler in certain industries.

3.0 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.

3.1 EVALUATION OF "MALJAT" LIMESTONE FILLER QUALITY BASED ON CHEMICAL COMPOSITION

According to the results presented above, limestone from "Maljat" – Danilovgrad 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 and C quality, while for the 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; it is among the highest I class in accordance with market and standard requirements (6, 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 content it is in quality category IV and V in accordance with market requirements imposed by standards (SRPS B.B6.020); it can be used for production of mineral fertilizers since its quality is in accordance with manufacturer's requirements (Azotara Pančevo); in production of cattle feed, it is among high quality raw materials in accordance with market requirements ("Official Gazette of the Republic of Serbia" 31/78, 6/81, 2/90, 20/00). Taking into account only the chemical composition, limestone Maljat can be potentially used in pharmaceutical and cosmetics industry (SRPS B.B6.034), but these industries for their needs requires great fineness of particles (90% -10μm). This large-scale fineness of grinding is technically difficult to do and too expensive. Because of that, these industries, most commonly are used PCC (precipited calcium carbonate).

Limestone from "Maljat" – Danilovgrad deposit cannot be used:

- for neutralization of acidic soils; because of the increased content of P_2O_5 as biogenic element, the content of which are very strictly defined ("Official Gazette of the Republic of Serbia" 60/2000).

3.2. EVALUATION OF "MALJAT" – DANILOVGRAD 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 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 "Maljat" 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; for production of mineral fertilizers "Azotara"- Pančevo does not define size classes limestone should meet for this purpose. For production of cattle feed the required fineness of limestone filler is 100% of -100μm. For pharmaceutical and cosmetics industry required fineness of particles is 90% of -10 μm. This large-scale fineness of grinding is technically difficult to do and too expensive. Because of that, these industries, most commonly are used PCC (precipited calcium carbonate).

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.

4.0 CONCLUSION

Limestone from "Maljat"- Danilovgrad deposit according to its physical-chemical properties belongs to high quality carbonate raw material with high content of $CaCO_3$ of 99.22%, and low content of $MgCO_3$ of 0.55% 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; glass industry; production of mineral fertilizers; 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, sugar industry, metallurgy, for production of mineral fertilizers, in production of cattle feed and for neutralization of acidic soils. However,

although limestone-Maljat does not meet the highest standards, it can be used for the production of paper and glass.

Due to high content of biogenic elements P_2O_5 (0.0312%), "Maljat" limestone cannot be used 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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4.0. ZAKLJUČAK

Krečnjak iz "Maljat" - Danilovgrad ležišta u skladu sa svojim fizičko-hemijskim osobinama spada u visoko kvalitetne karbonatne mineralne sirovine sa visokim sadržajem CaCO3 od 99,22 % i niskim sadržajem MgCO3 od 0,55 % i silikata (SiO2 0,16 %) . Ispunjava zahteve standarda za korišćenje kalcijum karbonata , kao punila u industriji boja i premaza ; industriji papira; gume i PVC industriji; Industriji stakla; proizvodnji mineralnih đubriva ; industriji livenja; industriji šećera i metalurgiji . Prema tražnja na tržištu i standardima pripada kvalitetnoj sirovini u industriji boja i lakova , gume i PVC , livnicama , industriji šećera , metalurgiji, za proizvodnju mineralnih đubriva , u proizvodnji stočne hrane i za neutralizaciju kiselih zemljišta. Međutim, iako krečnjak- Maljat ne zadovoljava najviše standarde , može se koristiti za proizvodnju papira i stakla.

Zbog visokog sadržaja biogenih elemenata P2O5 (0.0312 %) , " Maljat " krečnjak se ne može koristiti za neutralizaciju kiselih zemljišta .

Dobijanje širokog spektra filera za razne industrijske grane će obezbediti proizvode koji su skuplji po jedinici mase od proizvoda koji su korišćeni do sada i do 10 puta

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LITERATURE

[1] Izveštaj o ispitivanju krečnjaka sa područja Bjelopavlića Crna Gora, za primenu kao punioca u različitim granama industrije, Arhiva ITNMS, Beograd, 2011.
[2] http://geology.com/usgs/limestone/
[3] Mihajlović S.: 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] http://en.wikipedia.org/wiki/Filler_ 28materials% 29%
[8] C.A. Young, J.D. Miller, Int. J.: Miner. Process., 58 (2000) 331-350.
[9] www.minweb.co.uk / carbonates / calcite.html
[10] http://webmineral.com/data/Calcite.shtml
[11]. http://en.wikipedia.org/wiki/Calcite,
[12] Radica Milosavljević: "Metode ispitivanja mineralnih sirovina u pripremi mineralnih sirovina", Rudarsko-geološki fakultet Beograd, 1974.
[13] Lešić Đ., S. Markovic: "PMS-Priprema mineralnih sirovina", Beograd, 1968.
[14] Ćalić N., :"Teorijski osnovi pripreme mineralnih sirovina", Beograd, 1990.
[15] J. Pavlica, Draškić D.,: "Priprema nemetaličnih mineralnih sirovina", Rudarsko-Geološki fakultet, Beograd, 1997.

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