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## POTENTIAL OF CARBONATE RAW MATERIALS OF GRAČANICA, DEPOSIT "SKLOP"

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### ABSTRACT

Mineral resources as natural resources constitute the backbone of the development of the national economy of each country, and their valorization should be classified into its strategic development plans. Polyvalent industrial branches of the economy today are unthinkable without adequate supply of raw materials, analysis of raw material base, their preparation and processing, technology of breeding and possible application.

Due to the geological structure of the municipality of Gračanica, carbonate raw materials are one of the most important non-metallic mineral raw materials. In the territory of the municipality of Gračanica there are numerous areas with deposits of carbonate raw materials (architectural and constructional and technical-construction stone), among which the "Sklop" deposit occupies the most important place. This paper presents the geological characteristics, types of carbonate raw materials, deposits, reserves, quality and potentiality.

Key words: *carbonate mineral raw materials, building stone, technical-construction stone*

### INTRODUCTION

In the geological structure of the Gračanica field, carbonate rocks have the highest presence and participate with about 65%, and are presented mainly in limestone and cracked and marlaceous limestone.

These rocks so far valleys have been valorized through use in construction, as a technical-construction or architectural and constructional (decorative) stone, and very little are used as raw materials for obtaining carbonate fillers.

The most important deposits of carbonate raw materials in Gračanica, primarily technical-construction (decorative) stone, were discovered in the upper and paleocene-eocene carbonate deposits at the limestone deposit "Drijenča / Sklop"

The limestone is a sedimentary carbonate rock built basically by calcite. The most common limestone admixtures are dolomites, calcedon, quartz, clay minerals, volcanogenic material, etc. Limestone deposits originated mainly in the sedimentation process.

Cretaceous sediments have a widespread distribution and occupy about 10-15% of all sedimentary crevices of the earth's crust. Technical-construction stone is a carbonate mineral raw material which practically has unlimited potential in the area of Gračanica, so that it is rightfully said that the municipality of Gračanica is rich in technical-construction stone and is one of the most important non-metallic mineral raw materials. Within the ore region of "Drijenca", larger deposits of technical and construction stone of limestone were discovered, but given the geological structure of this ore region, the number of technical and building stone deposits could be significantly higher. Since it is a low-cost raw material that does not suffer from over-transport, the key factor for viable exploitation is the location of the deposit, ie the geological formations and their potentiality.

The aforementioned carbonate rocks are valorized, mainly through use in construction as a technical-construction or architectural-construction stone, and they are very little used as raw materials for the production of molten metal in the metallurgy, the production of mortars and lime. However, the special valorization of the rocks of carbonate composition, primarily limestone, is the production of carbonate fillers and their application in various branches of industry. By developing the chemical industry and improving the production technology, the possibilities of using carbonate fillers in various branches of the economy are significantly expanded: the construction industry, the paint and varnish industry, the pharmaceutical and cosmetic industry, the food industry, the rubber industry, the paper industry, cables, polyvinylchloride, mineral fertilizers, etc. [1,2,3,4].

For the application of limestone in the mentioned branches of industry, the quality requirements (degree of purity) are very high, so that some amount of limestone is defined as economically interesting, it is necessary to determine the conditions that existed in their education (genetic) and then qualitative properties in terms of the presence of harmful components, the content of certain useful components, or the degree of limestone purity.

#### GENERAL INFORMATION ON THE OWN RESION

Within the territory of the Municipality of Gračanica, there are deposits of technical building stone limestone, they are more concentrated on the site "Drijenča" and "Sklop" in Gračanica and Dobarovci at the site "Greblje".

According to the geological structure of the area of Gračanica, unlimited geological reserves of triassic, cretaceous and tertiary limestone have been determined, which are exploited and valorized through several open pit mines. Bearings were opened at the sites "Sklopa" and "Greblje" in Dobarovci.

In the morphological view, the Drijenča limestone deposit is located on the hilly area of the southern slopes of the Trebovica Mountain with an average altitude of 250-400 m.

From the hinterland towards the north stands the Vis hill, which at the same time represents the highest peak of Trebovac Mountain.

From the west and south-west only the deposit is limited by the stream Drijenca and asphalt, while the eastern and northern sides are a limestone massif, which is gradually covered with low vegetation and forest. The maximum area of the terrain is 372 m, the lowest is 250 m, so the maximum hypsometric difference is 122 m. The terrain from this ridge gradually descends to the south in the valley of the Sokoluša river and its tributaries with an altitude of about 250 m above sea level; built mostly of clastite and carbonate of the middle Miocene, and above the valley there are several higher elevations built from the limestone paleocene-eocene and upper chalk.

In the field, several latitudes of the direction of provision of the northwest-southeast and northeast-southwest are formed, usually in terrains built from the cluster of the middle miocene in the wider area. A short flow of occasional and constant streams is formed along these valleys. These smaller densities are predominantly predisposed by the erosion of relatively softer clastic deposits of the middle miocene.

The area of the approved exploitation field of these deposits is about 20 hectares [5].

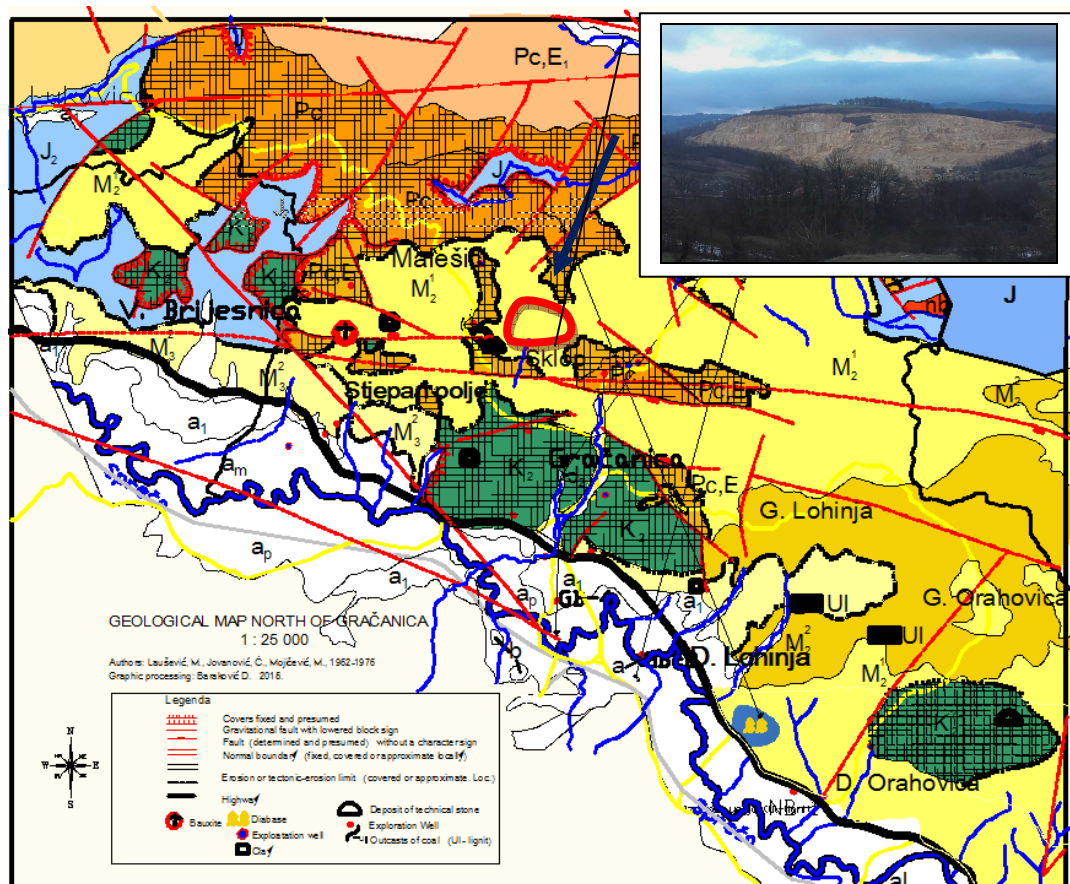


Figure 1. Geological map north of the river Spreče showing the locality of the technical building stone deposit "Sklop".

## GEOLOGICAL CHARACTERISTICS OF DEPOSITS

Detailed geological mapping of the wider exploration area "Drijenca" / Sklop, stratigraphic units of Jurassic oolitic melange, upper chalk, paleocene - lower eocene and deposits of the upper Miocene tectonic floor were isolated.

The deposits of the upper chalk are represented by plate-like marlstone limestone, breccia limestone and plate-like dark red marlstone limestone.

Upper-Miocene (Sarmatian) deposits are represented by limestone, marl, conglomerates and pedestals. They are located north of the exploration area and on limestone outflows the limestone development is determined.

The carnations are yellowish gray to light gray, uniform composition, homogeneous texture and fine-grained structure. It reacts vigorously on decomposed hydrochloric acid.

On the tectonic contact of the upper and paleocene-eocene deposits, it is open with the Drijenča quarry, with the orientation of the exploitation works approximately east - west. The quarry is a hilly type, with a total hipsometric difference of about 75 m. The deposit is open with 6 exploitation floors (260, 275, 290, 305, 320 and 335 m). Limestone can be distinguished in limestone, which differ in color by color, the presence (absence) of layering, and the following could be recorded:

- Surface rubbing material, which is present in the eastern part of the deposit
- Massive white limestone, with a disintegrated surface

- Blonde disintegrated plate limestone
- Dark red marble limestone with visible primary layering.

## STRUCTURAL - TECTONIC CHARACTERISTICS OF THE DEPOSIT

The tectonics of the deposits were undoubtedly influenced by the very turbulent orogenic events that this area was exposed to during the geological evolution. The mere presence of 4 striking faults in the wider area suffices to support the fact that it is a very complex tectonic location. This is primarily the fault of Klokočnica - Dobrovci (providing I - Z). During field prospecting and mapping of the terrain, a number of flip charts were identified that had a direct impact on the degree of damage and subsequent exogenous processes. The marking disorder of providing SI - SW (245 ° / 40 °), the Drijenča limestone deposit is divided into the eastern and western parts which differ in each other according to the physical and mechanical characteristics, color and degree of tectonic damage:

I - the eastern part of the yellowish-yellow disintegrated limestone

II - the western part of the deposit consists of a light gray massive limestone.

The formation of limestones and deposits at this locality is related to the marine environment for the coastal belt. The limestone of the limestone, the coagulation and purity of the carbonate sediments, indicates that the precipitation was carried out in a calm environment without major flows and interruption in sedimentation.

It is an organogenic sedimentary type of bearing, the most common forms of which are layered.

## RESEARCH WORKS, ORE RESERVES AND QUALITY

Given that the current level of research has determined the spatial position of the limestone deposits of these deposits, it was primarily focused on the potential of this raw material, that is, on the mineral reserves and the quality of mineral raw materials based on the latest laboratory tests in terms of potentiality and application in different branches of industry.

Research works included: geological works and application of laboratory test results. Geological and mining explorations, the limestone deposit "Drijenča", was opened with 5 exploitation floors. In the framework of exploitation surveys in 2016, four (4) wells were drilled. The boreholes wanted to determine the distribution of limestone deposits to the level of 250 m. Investigative scaffolds are mostly worked in an unopened part of the deposit, due to the consolidation of the thickness of the surface cover and the taking of samples for determining the physical and mechanical characteristics of the limestone.

Earlier research by visual tracking of spawns, the boundary between Paleocene-Eocene limestone and Miocene and Cretaceous deposits has been established, which has disrupted the mining body.

## ORE RESERVES DEPOSIT LIMESTONE "SKLOP"

Based on the calculation of reserves by block method, the following results were obtained:

Table 1. Overview of the deposit reserves of technical and construction stone deposit "Assembly"

Reserve category	Reserve (m <sup>3</sup> )	Share (%)	Usage (%)	Reserve block mass (m <sup>3</sup> )
A	349.499	10,75		
B	2.310.602	71,05		
C <sub>1</sub>	592.081	18,20	75	444.060
„A+B+C <sub>1</sub> “	3.252.182	100,00		3.104.161

## QUALITY OF MINERAL RAW MATERIAL

The methodology for tracing investigative works was based on taking samples from exploitation floors, exploratory rockets and wells. Assessment of the quality and usefulness of limestone was obtained by the synthesis of the results of the performed tests.

The test methodology was contained in the following:

- Mineral - petrographic tests
- Chemical tests
- Physical - mechanical testing.

Mineralogical petrographic analyzes have determined that the rock is light-colored, partially yellowish and with small veins and cavities filled with calcite. It is very compact and firm, irregular fracture with jagged and sharp fracture edges. The texture is massive, the structure is crystalline - grainy. It reacts violently with hydrochloric acid.

It contains very little quartz and iron oxide that is lemonade, which gives the claret a yellowish color. Based on samples from open profiles, the mean chemical composition of the limestone of the "Sklop" deposit was determined. Table 2.

Table 2. Chemical analysis of mineral raw materials

Mark	Value Mean (%)
CaO	54,47
SiO <sub>2</sub>	0,41
Al <sub>2</sub> O <sub>3</sub>	0,36
Fe <sub>2</sub> O <sub>3</sub>	0,34
MgO	0,41
G.Ž.	43,82
S	0,09
CaCO <sub>3</sub>	97,64

Based on all available data, the mean values for all parameters that determine the physical and mechanical characteristics of the rock mass are calculated and the average values are obtained:table 3.

Table 3. Physical-mechanical characteristics of mineral raw material

Pressure Strength		Resistance to wear (cm <sup>3</sup> /50cm)	Resistance to wear L.A. (%)	Volume weight (t/m <sup>3</sup> )	Water absorption (%)	Porosity (%)	Resistance to cold	The content of sulphides and sulphates (%)
In dry condition (MPa)	In water saturated (MPa)							
127,05	123,2	16,5	7,0	2,78	0,21	0,60	Resistant	0,02

On the basis of the tests carried out, limestone from the area of the ore region "Sklop" can find application in various industrial branches such as:

- pharmaceutical and cosmetic industry, paints and varnishes industry, paper, rubber and PVC, casting industry, sugar industry, glass production, metallurgy and mineral fertilizers, as a composite material in the production of concrete mixtures for cement concrete and in the service of ecology, in reducing the emission of harmful gases into the atmosphere as limestone powder in the desulfurization process in thermal power plants.

## POTENTIAL OF CARBONATE RAW MATERIALS „SKLOP“

When it comes to the potential of the carbonate raw materials of this area as a technical-construction stone, taking into account the geological structure, it can be concluded that it is virtually unlimited. Physico-mechanical tests of limestones from individual deposits where the exploitation of technical-construction stone (Sklop) is made, some deposits where detailed geological explorations were performed (Dobarovci), as well as some phenomena on which samples were taken for tests (D.Orahovica, Drijenča "), the possibilities for their use for technical and construction purposes have been proved. The technical-construction stone of the carbonate composition in the investigated deposits is of good quality, but rarely of the highest quality that would meet the most stringent requirements for wearing high layers of roads with high loads or for fast lanes.

From the point of view of the use of carbonate raw materials as a filler, the estimation of potentiality is based on various properties that can be considered specific for a particular deposit. The assessment of potentiality relies, basically, on geological data on characteristic features and geochemical data on which depends the possibility of limestone application in certain branches of industry. In addition to these, to assess the potential of limestone, there are other characteristics that can be significant for the application of limestone in certain branches of industry, such as physical and mineralogical and technical characteristics. The quantification of the parameters for the ranking was based on the possibility of applying it in the appropriate industries, as M-possible, L-limited, VL-very limited and N-not applicable.

The basic restrictions on the use of limestones from individual deposits from the area of the ore region in certain branches of industry are predominantly due to the degree of limestone whiteness and chemical composition, ie the content of useful and harmful components.

On the wider area of Gračanica on a relatively small area, there are deposits and occurrence of carbonate raw materials such as: technical rocks, "Sklop", Doborovci, Monj, etc. The mentioned mineral resources were subject to certain geological and mining research during the larger part of the 20th century. Exploitation on some of the traps was organized in some traps.

The prognostic evaluation of any natural solid mineral resource of a certain area, and also of non-metallic raw materials in the wider area of Gračanica, is based on the specific characteristics of individual types of deposits located in that area or its vicinity and in similar geological and geotectonic conditions.

General criteria for mining, based on which the mineragenetic - prognosis is made, was defined by [6], and mostly developed for the purposes of forecasting metallic mineral resources. However, some of these criteria are the basis for a forecast assessment and non-metallic mineral raw [7,8,9], and therefore carbonate raw materials. Criteria of mineragenetic - prognostic evaluation of non - metallic mineral resource resources have so far been generally poorly considered. From the aspect of the resources of non-metallic mineral raw materials, the following significant prognostic criteria were set out:

- Stratigraphic
- Litological
- Paleogeographical
- Structural
- Technological
- Geological and economical

In determining the category of potentiality of carbonate raw materials in the area of the Gračanica area, it was noted that this area was not systematically researched from the aspect of non-metallic raw materials, but in the course of the investigation works proceeded from the already known phenom

on the field, and afterwards approached detailed research. Therefore, the level of research of non-metallic raw materials is not the same, neither is their potential.

Based on the consideration of the criteria for the assessment, the following categories of potentialities of the wider area of Gračanica were identified: [10].

1. Areas of great potentiality,
2. Medium-potential areas, i
3. Areas of vague potentiality.

In the field, which is characterized by high potentiality, a certain mineral resource is detailed in both the genetic conditions of the plant and the technological characteristics, and there are also open deposits and occurrences of these non-metallic raw materials, such as the "Sklop" deposit, table 4. [11].

Table 4. Degree of potentiality and spatial distribution of limestone

Type of raw material	Location	Character of resources	Mineral reserves	Potentiality
<b>LIMESTONE</b>	„Drijenča“	Deposits	A+B+C <sub>1</sub> 4.600.000	<b>BIG</b>
	„Sklop“	Deposits	A+B+C <sub>1</sub> 3.250.000	
	„Greblje“	Deposits	A+B 1.250.000	

When it comes to the potential of the carbonate raw materials of this area as a technical-construction stone, taking into account the geological structure, it can be concluded that it is virtually unlimited. Physico-mechanical tests of limestones from individual deposits where the exploitation of technical-construction stone (Sklop) is made, some deposits where detailed geological explorations were performed (Dobarovci), as well as some phenomena on which samples were taken for tests (D.Orahovica, Drijenča "), the possibilities for their use for technical and construction purposes have been proved.

The technical-construction stone of the carbonate composition in the investigated deposits is of good quality, but rarely of the highest quality that would meet the most stringent requirements for wearing high layers of roads with high loads or for fast lanes. From the point of view of the use of carbonate raw materials as a filler, the estimation of potentiality is based on various properties that can be considered specific for a particular deposit.

The assessment of potentiality relies, basically, on geological data on characteristic features and geochemical data on which depends the possibility of limestone application in certain branches of industry. In addition to these, to assess the potential of limestone, there are other characteristics that can be significant for the application of limestone in certain branches of industry, such as physical and mineralogical and technical characteristics. The quantification of the parameters for the ranking was based on the possibility of application in the appropriate branches of industry, such as: M-Possible, L-Limited, VL-Very Limited and N-Not applicable, Table 5.

Basic Limitations of Limestone Application from Individual Bearings from the Ore Area in certain branches of industry are predominantly conditioned by the degree of limestone whiteness and chemical composition, ie by the content of useful and harmful components [12,13].

Carbonate fillers are a very important raw material that can be used in very different industrial branches. The area of Gračanica is distinguished by the presence of mineralogical and chemically very clean limestone, which have so far been explored mainly as architectural-construction and technical building stone. Recent research, both terrain as well as mineralogical, petrochemical, spectrochemical and technological tests on 4 deposits and the occurrence of limestones, showed the high quality of this mineral resource, with the limestone from almost all deposits and /or phenomena can be used in the food industry and sugar, most in the paint and varnish industry, rubber and plastics, metallurgy, and

foundry. Several deposits and phenomena contain a high quality limestone that can be used in the paper, glass, pharmaceutical and mineral fertilizers industry.

Table 5. Potential application of limestone from the area of Gračanica as a filler (M-possible, L-limited, VL-very limited, N-not applicable;

Deposits	INDUSTRIAL GRAPE						
	Paints and varnishes	Paper	Rubber and PVC	Glass	Sugar industry	Fodder food	Pharmacy and cosmetics
Drijenča	M	M	M	L	M	VL	M
Greblje	M	M	M	L	L	VL	M
Sklop	M	M	M	L	L	VL	L

All deposits and phenomena included in Table 4 are disposed within the oleate expressed to the mineral raw material potentials of the wider area of Gračanica, Figure 2.



Figure 2. Map of the potential of limestone as a carbonate raw material in the area of the municipality of Gračanica



By determining the potentiality of the area of carbonate raw materials through oleate of the mineral raw material potential of the wider area of Gračanica, a more transparent and clearer spatial distribution of carbonate mineral raw materials is given, which is extremely important for future spatial planning in the area of Gračanica, urbanization, valorisation of natural resources and measures for the protection of nature and the environment.[4]

## CONCLUSION

In the area of the municipality of Gračanica, several types of carbonate raw materials have been discovered, whose economic potential is clearly visible when looking at the data on reserves of carbonate resources in this area. The shelves most promising for the production of carbonate fillers are active deposits of technical-construction stone, where the yield in the block is about 20%, while the rest of the rock mass is not fully and / or at all used at this time either as a carbonate filler or as another product .

Application of carbonate fillers with potential is in the cement and concrete production industry. Namely, the concrete with high content of carbonate fillers with the appropriate granulometric composition generally improves the concrete strength characteristics compared to conventional concrete, where the same ratio of water, cement and cement type is.

In particular, it is a good possibility for waste in some quarries of technical-construction stone to be used for concrete mixtures [9]. This industry requires pure carbonate, but also a relatively inexpensive product.

Further geological testing and complete characterization of limestones from this area should be carried out in accordance with legal regulations [10], but with their rational use. This would involve systematic research and testing on a large number of samples, in order to define different levels of limestone that can be used in the most rational and appropriate manner.

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