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# **A contribution to the research of Mostar miljevina with special reference to frost resistance**

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**Abstract**: The paper presents the freshwater limestone Mostar miljevina (miljevina). In the diagenesis process, it acquired a specific orientation and structure, which gave it specific physical properties that geologically older, compact (dense) limestones do not have. The results of the previous tests of miljevina from the Mukoša deposit near Mostar and from several buildings in Mostar are presented. Miljevina is less crystalline, less dense, and thereby less resistant to the processes of chemical deterioration and deterioration caused by crystallization. Due to the high absolute porosity of the open pores, miljevina has high moisture absorption and pronounced capillary water absorption, so it was not desirable to install it on surfaces directly exposed to wetting by rain and gusts of wind, but it was protected by facades, with the use of another type of stone in the part of the building in contact with the ground.The second part of the paper presents the results of testing miljevina as part of the graduation thesis, especially frost resistance, with appropriate conclusions and comparisons with previous results.

**Keywords**: freshwater limestone, miljevina (stone), Mukoša (quarry), frost resistance

# **Prilog istraživanju mostarske miljevine s posebnim osvrtom na postojanost na mraz**

**Sažetak**: U radu je prikazan slatkovodni vapnenac mostarska miljevina (miljevina), koji je u procesu dijageneze zadobio specifičnu orijentaciju i strukturu, što mu je dalo specifična fizikalna svojstva, koja nemaju geološki stariji, kompaktni (gusti) vapnenci. Prikazani su rezultati dosadašnjih ispitivanja miljevine iz ležišta Mukoša kod Mostara i iz nekoliko objekata u Mostaru. Miljevina je manje kristalna, manje gusta, pa time i manje izdržljiva na procese kemijskog propadanja i propadanja uzrokovanog kristalizacijom. Zbog visoke apsolutne poroznosti otvorenih pora miljevina ima visoko upijanje vlage, te naglašeno kapilarno upijanje vode, pa ju nije bilo poželjno ugrađivati na površine izravno izložene kvašenjem kišom i naletima vjetra, već je zaštićivana fasadama, uz primjenu druge vrste kamena u dijelu objekta u dodiru sa tlom. U drugom dijelu rada prikazani su rezultati ispitivanja miljevine u okviru diplomskog rada, posebno postojanosti na mraz, uz odgovarajuće zaključke i usporedbe sa ranijim rezultatima.

**Ključne riječi**: slatkovodni vapnenac, miljevina, Mukoša, postojanost na mraz

## **1. INTRODUCTORY NOTES ON FRESHWATER LIMESTONES FROM THE MUKOŠA DEPOSIT NEAR MOSTAR**

About 30 scientific and professional papers have been published and a doctoral dissertation has been made by the authors of this paper on freshwater (lacustrine, tufaceous) limestones, and a book on this topic has just been published [1,2,3,4,5].

In addition to the well-known freshwater limestones from Bosnia, "bihacit" (near Bihać), "plivit" (near Jajce), and "bosanska mošćanica" (near Zenica), three lithostratigraphic units that have a common marly-clayey and limestone component are identified within the Neogene deposits in Herzegovina, and they differ in the identified characteristic fossils, the content of coal intercalations, and the presence of different types of limestone. The first two units belong to the Miocene ( $M_{23}$  and <sup>2</sup>M), while the third one is not further analyzed within the Neogene (N).



Figures 1-2. Simplified map of a part of Herzegovina with the three lithostratigraphic units with a common marly-clayey and limestone component, left; part of unit number 1 with the Mukoša deposit near Mostar, right [4,5].

Lithostratigraphic unit number 1 is mapped in the wider area of Mostar (Ortiješ, Buna, Hodovo and Rodoč), on the Basic Geological Map (BGM) under the name marls and conglomerates with clivunellas (M2,3) and is named after the discovered fossil freshwater snail Clivunella katzeri. Two subtypes of finely bedded oolitic limestone of different grain sizes are identified, with local names tenelija, coarse-grained, oolitic limestone, and miljevina, finegrained limestone. Although slightly degraded by cracks and fissures, they are quite compact, strong and tough, and represent a good raw material for the production of dimension stone, so they have been used in construction since ancient times.

According to [4,5], Šaravanja called this miljevina Mostar miljevina, and the miljevina from the Posušje region - Posušje miljevina due to their essentially different mineralogicalpetrographic, chemical and physical-mechanical properties, confirmed not only by test results, but also by different uses. He named the tested muljika from the Tomislavgrad municipality Tomislavgrad muljika, in order to distinguish it from other varieties of muljika from southwestern and central Bosnia. Since this paper only deals with Mostar miljevina, the name milievina is used in further text.

More than half a century ago, Čičić, S. mapped this terrain and called the deposits limestone marls (1960). In the 1960s, Tufegdžić, V. and Hamović, J. from the Faculty of Civil Engineering, University of Sarajevo examined the physical and mechanical properties of this stone and its durability.

Valuable data on the properties of stone were obtained during the restoration and conservation of the foundation and arch of the Old Bridge (Mostogradnja, 1963), when a team of experts headed by prof. Luka Marić from the Faculty of Mining, Geology and Petroleum Engineering in Zagreb studied in detail the mentioned freshwater limestone varieties, separated them by structure, texture, mineralogical-petrographic and chemical composition, and made a geological-petrographic evaluation of the stone built into the Old Bridge, but also the Mukoša deposit. In his paper "On the stone from which the Old Bridge in Mostar was built" (1972), prof. Marić described in detail the damaged blocks on the bridge and microscopically examined samples of two limestone varieties. The stone is classified in the group of so-called tufaceous limestones, namely a fine-grained (oolitic) agglomerate of white color and homogeneous variety of slightly yellowish color [6,7].

According to BGM, sheet Metković (Raić and Papeš, 1971), the rock on the deposit site is described as "calcareous marl and marl", and the age of these deposits was determined by the discovery of the freshwater snail Clivunella katzeri. In 1979, prof. Crnković determined that it is (a type of) limestone. Several unfavorable properties of these deposits, as the result of variable sedimentation conditions, have been observed - sudden changes in the grain size of the granular material, high porosity or zones with larger or smaller voids and frequent intercalation, i.e. alternation of tenelija and miljevina interbeds, which are very difficult to distinguish in the field, based on different compressive strengths and water absorptions, with a very large variation in test results, especially miljevina [8].

The banked structure of freshwater limestones is confirmed, with changes in both vertical and horizontal terms. Banks of yellow-gray fine-grained miljevina alternate with coarse-grained tenelija. In the identified layers, intercalations of miljevina can be found in tenelija and vice versa. Transitional layers, which have the characteristics of miljevina and partly of tenelija, are identified.



Figure 3. Block diagram of the tenelija and miljevina deposits in the Mukoša deposit near Mostar [9]

It is evident from Figure 3 that the miljevina is considerably more common in the deposit (about 95% of the total mass) than the more valuable and expensive tenelija, which occurs within a complex bank, with lenses of miljevina 1-10 cm thick, and the bank is overlain by miljevina with another five thin layers of tenelija of significantly pronounced stratification [10]. So, tenelija

makes the upper layer of rock that follows the configuration of the terrain in layers 0.6 to 2.0 m thick with a clearly visible sharp transition to the limestone of the lower layer - miljevina. During the excavation, tenelija was first found at a depth of about 6 m below the deposits of miljevina, which is less degraded by cracks and of higher quality than that on the terrain surface [8,11].

#### **2. COMPARISON OF TEST RESULTS OF FRESHWATER LIMESTONES**

Based on the analysis of the available test results of tenelija, its properties can be said to be relatively well tested. Unfortunately, these tests were only concerned with the stone extracted from the Mukoša deposit, and not to the stone installed in various buildings, except for the testing of the remains of the Old Bridge. The authors of the paper have published several papers on this topic, of which a particularly significant scientific paper was published at the 3<sup>rd</sup> International Symposium on Stone "Herzegovina - Land of Stone" held in Mostar in 2018 [3].

When it comes to miljevina, the available number of results is far smaller than for tenelija, and so for testing of stone from the same deposit, and only the results of testing miljevina installed in the NAMA building in Mostar were available before the doctoral thesis of K. Šaravanja was developed.

An analysis of all available test results established their very high variability for various reasons as a product of a number of uncertainties that accompany stone as a building material and test results:

In the last 60 or so years, the tests have been conducted by different laboratories and different testers in them (GFS-GTF, IGH-Mostar, later IGH Mostar, IGH Zagreb, FMGCE Tuzla, FMGPE Zagreb, Cerberus Tuzla, etc.);

the tests were performed on samples of various shapes and dimensions (cubes, cylinders, prisms);

the tests were performed perpendicular to the strata, in the direction of the strata, and in many cases the stratification was not taken into account;

the tests were performed according to different standards, especially frost resistance testing (different numbers of freezing and thawing cycles at different temperatures, as well as crystallization tests with sodium and magnesium sulfate);

sampling from the quarry was differently related to the time elapsed after extraction (stone just extracted or being left for some time);

the samples were taken from various places and layers in the Mukoša deposit with visually noticeable variations in structure, porosity or color, which resulted in very large variations in strength, porosity and other properties of tenelija and miljevina.

According to [4], the term "new" (stone) was used for all freshwater limestone samples from the quarry, and the term "old" (stone) for samples from buildings, as was previously used for tenelija. The same terms were also used in [27], and the results of this research are presented further in this paper.

Table 1 gives a comparison of the intervals of average values of the results of freshwater limestones from Herzegovina installed in buildings ("old limestones"): Mostar miljevina, Posušje miljevina and Tomislavgrad muljika.

Table 1. Comparison of average values of the results of installed freshwater limestones of Herzegovina [4,5]



#### *NOTES:*

*The prefixes of the average test results give the number of tests, e.g. 20.5<sup>2</sup>*

*\* no peeling, crumbling and cracking were observed;*

*\*\* peeling, crumbling and cracking were observed already in the 12th cycle, some samples completely disintegrated by the end;*

*\*\*\* mass loss is not shown because the sample mass increased after the end of the 5th cycle; washing out was conducted with running water for 24 hours, with additional "boiling" of the samples at 60 °C and drying; it was not possible to wash out the entire amount of sodium sulfate from the samples;*

*\*\*\*\* mass loss on 2 out of 3 samples could not be shown, and the loss of the third sample was 12.3%;*

*\*\*\*\*\* 5 samples were tested, of which 2 samples began to disintegrate after 1 cycle, 2 samples after 2 cycles, and the fifth sample after 3 cycles; The average mass loss after 5 cycles is 6.5%;*

*The value of the water permeability coefficient tested with a hydraulic gradient of 30, corresponding to a water column height of 3 m above the tested sample, which approximately corresponds to the water level conditions of the Neretva River at the Old Bridge (DIN 18130), ranged from 4.83-34.4 x 10-04 .*

### **3. COMPARISON OF TENELIJA AND MILJEVINA**

The extent to which tenelija and miljevina are intertwined in the Mukoša deposit near Mostar was probably best expressed by Hivzija Hasandedić, who wrote that "all Mostar mosques are built of stone, namely mainly of miljevina called tenelija, which is also called mukla (dull) miljevina [12].

Tenelija is a coarse-grained oolitic limestone, with a homogeneous (massive) texture and high porosity. Its strength and durability depend on the grain size (coarse and fine-grained ooids) and natural porosity (coarse tenelija and fine tenelija) [14]. It is easy to cut and dress, any motif can be carved into it. It quickly absorbs moisture and hardly removes it, it is sensitive to fire, and its color varies from whitish, grayish to yellowish, depending on age, humidity or when it is just extracted from the quarry.







Figures 6-7. SEM images of different structures of tenelija (left) and miljevina (Source: Institut LGA) [15,16,17]

Miljevina differs from tenelija in texture and structure, which is why the effect of external factors on these varieties is different. Unlike tenelija which has a concentric oolitic structure, miljevina has a dense, submicroscopic fine-grained structure in which there is little or no ooids, in which cementation and recrystallization of calcite (dense limestone) has not taken place [15]. This is why it retains moisture for a long time, and the effect of temperature changes and ice causes surface loosening and deterioration of the stone [10,15].

Miljevina has weaker physical and mechanical properties than tenelija. The grains are supported by mud (mudstone), due to which it retains moisture for a long time, and the effect of temperature changes and ice causes surface loosening and deterioration of the stone [16,18]. According to [6] considering the grain size, miljevina can be classified as a silty, and possibly also clayey fraction.

# **4. MILJEVINA INCORPORATED IN BUILDINGS ("OLD MILJEVINA")**

## **4.1. Simplified petrographic description (macroscopic and microscopic determination)**

Mineral-petrographic and chemical tests of the stone sample were performed according to BAS EN standards 932-2:2002, 932-3/A1:2011, and standards JUS B.B2.009, JUS B.B2.010 and JUS B.B8.042 in the company Cerberus d.o.o. from Tuzla in 2020.

Miljevina from the Mukoša deposit was determined as microcrystalline limestone with microcrystalline (to cryptocrystalline) structure (Cerberus, Tuzla), and two samples from abandoned buildings in Mostar as crystalline porous limestone, with crystalline structure (Cerberus, Tuzla), or as dismicrite, with fine-grained structure and stratified structure (IGH, Zagreb) [4,5].

#### **4.2. "In situ" tests**

 Non-destructive "in situ" tests with Schmidt hammer (sclerometer) were carried out at the site of an abandoned residential building near the Health Center in Mostar in 2020 to obtain compressive strengths. The compressive strengths of the hardened surface part of the monument of about 35 MPa (Profile Mostar1), and about 38 MPa (Profile Mostar2) were obtained from the diagram.



Figures 8-10. Compressive strength testing with a sclerometer of an abandoned residential building near the Health Center in Mostar (Profile Mostar1 and Profile Mostar2) (processed by: K. Šaravanja) [4,5]

Recording with a manual microscope and macroscopic and microscopic determination were performed on the stone sample taken (M1).

#### **4.3. Chemical testing of stone and patina on stone**

 Chemical analyses of stone and patina for sample M1, conducted by the company Cerberus from Tuzla in 2020 confirmed that it is almost pure calcite, or limestone, with about 94% CaCO3 (Table 2).

Table 2. Results of chemical analyses of stone and patina on stone (old) miljevina - sample M1[4.5]



*Note: The contents of CaCO3 and MgCO3 in the table obtained by stoichiometry* 

#### **4.4. Physical-mechanical tests**

As part of the physical-mechanical tests of (old) miljevina, tests were carried out on a stone sample from the NAMA building in Mostar, as well as on a sample from an abandoned building near the Cathedral in Mostar (M2) IGH Mostar.

Table 3. Test results of the (old) miljevina sample from the NAMA building and the sample marked M2 [19,4,5]



*\* no peeling, crumbling and cracking were observed* 

Figures 11 and 12 show a compressive strength testing press with an adapter for centering smaller samples (left), with a detail of broken miljevina sample after testing.



Figures 11-12. Compressive strength testing press with an adapter

# **5. (NEW) MILJEVINA FROM THE MUKOŠA DEPOSIT NEAR MOSTAR**

 Visual inspection using a manual microscope, as well as "in situ" non-destructive testing (NDT) of the stone using the Schmidt hammer (sclerometer) were carried out at the quarry site.



Figures 13-15. Testing of (Mostar) miljevina (new one) from the Mukoša deposit near Mostar with a manual microscope and Schmidt hammer, along with visual inspection (photo: K. Šaravanja) [4,5]

#### **5.1. Petrographic description (macroscopic and microscopic determination)**

 Mineralogical-petrographic and chemical tests of the stone sample were carried out according to the previously mentioned standards in the company Cerberus from Tuzla in 2016. The texture of the tested sample is massive, and the structure is microcrystalline (to cryptocrystalline). Calcite is the main mineral (over 98%), so the rock is almost monomineralic. Finer grains of calcite (up to 0.2 mm) can be seen at the base of the rock, while the rest has a microcrystalline structure. Due to the minor part of the clayey-carbonate component, the base of the rock is opaque in some places. Terrigenous and metallic mineralization are not established. Fossil remains are not established. Rock: Sedimentary, carbonate, cohesive rock: limestone, microcrystalline.

## **5.2. Chemical analysis**

 Chemical analysis was performed at the company Cerberus from Tuzla, and at Mineral laboratories Canada, Laboratory Krakow in Poland in 2016.



*respectively.* 

Figure 16. Results of chemical analysis of (new) miljevina [20]

## **5.3. Physical-mechanical tests**

During the exploration of the deposit in 1998, samples were also taken for testing the (new) miljevina, which was done in IGH-MOSTAR. One sample was formed from the rock mass from cut R-1, and 2 samples from different parts of the deposit, so that the results apply to the entire deposit [19]. Table 4 presents the results of the tests carried out in IGH Mostar in 2016 from two neighboring deposits at the Mukoša site, from exploratory boreholes B-1, B-2, B-3 and B-4 and cut (PEE) (mark Revigrad1), as well as the testing of natural stone from exploratory boreholes B-1, B-2 and B-3 (mark Revigrad2). The obtained density test results differ from other results and correspond more to the obtained results of the (new) tenelija test. Table 4 shows the difference of the results obtained at the Faculty of Civil Engineering, Sarajevo in 2017, shown in the last column of the table.







*NOTES:* 

*\* density results correspond more to the density of "tenelija";* 

*\*\* there is no visible damage;* 

*\*\*\* samples did not show any changes in terms of peeling, crumbling and cracking. The solid structure of the samples remained unchanged, there is no change in the apparent volume of the test samples*

Table 5 provides an overview of the coefficients of softening of miljevina.

Table 5. Overview of coefficients of softening  $(C<sub>s</sub>)$  of (new) miljevina [4,5,17,21,23]



Here is a brief overview of some of the obtained test results from Table 4:

- Abrasion resistance test:

Tenelija and miljevina belong to markedly soft stone, where the wear resistance result according to Böhme for miljevina was as much as 65.6 cm $3/50$  cm $^2$ , which in the built structure means tendency to mechanical wear, rounding of sharp edges, etc. Strong winds that carry sand and dust can have a wearing effect on facade coatings;

- Frost resistance test:

- after 25 cycles of freezing and thawing according to the JUS B.B8.001 standard:
- in IGH-MOSTAR (2002) after only 3 of the planned 25 cycles carried out on 5 samples of miljevina, the test was stopped due to the occurrence of cracks and breakage of samples, with the conclusion that miljevina is unresistant to frost action);

High water absorption has a direct effect on reducing compressive strength in wetting conditions and on frost resistance. The reduction of compressive strength due to the presence of moisture in the stone is expressed by the coefficient of softening CS, which for miljevina was in the range 0.55-0.74, with the difference in relation to the tests of 2 series of miljevina samples for the company Revigrad, when it was 0.80-0.88 (2016), as a result of the obtained high density values, which better correspond to tenelija than to miljevina. In addition to the low CS, an indicator of the unsuitability of the use of miljevina in conditions of exposure to wetting is also the high saturation coefficient SC, i.e. a relatively small difference in water absorption in the process of saturation by boiling in water compared to the process under atmospheric pressure. When testing frost resistance, samples of miljevina were previously saturated with water by the process of boiling in water, which achieves 13% higher pore filling with water in relation to the process of saturation with water under atmospheric pressure (in tenelija this difference in saturation is 33%). In its fine-grained structure, water is retained longer, which creates conditions for the formation of ice lenses and it is thereby less frost resistant. A high SC greater than 0.80 indicates high hygroscopicity and most likely very easy ingress of moisture from the environment [24] which means that miljevina is highly sensitive to frost damage, i.e. it is not frost resistant. In old buildings with walls made of miljevina, the problem of increased moisture has always occurred, so they were protected with facades, with the use of another type of stone in the lower part of the building that is in contact with the ground (for foundations and basement), which is part of the construction tradition, the reason for which is the high absorption of milievina.

In the conditions of modern use of miljevina for facade cladding, the above-mentioned relations to wetting and moisture are markedly unfavorable, which is why stone cladding is protected with a highly water-repellent impregnating agent. It is important to assess and predict the mechanism of movement of water in the stone, both inside and on the surface, because most of the disintegration processes occur during water retention and drying, and not during the

period of absorption. The increased amount of water absorbed can be influenced by windborne rain, while wind gusts and air pressure can accelerate the rate and depth of water penetration into the stone [24,25,26].



Figure 17. Fracture of (new) tenelija and (new) miljevina samples and test termination after only 3 of the planned 25 cycles of freezing and thawing in IGH-MOSTAR in 2002 [26]

 crystallization test according to the JUS B.B8.002 standard with 5 cycles in saturated sodium sulfate solution: in "IGH-MOSTAR" (2002) out of 5 samples, 4 samples had mass losses of 5.8%, >5%, >10% and >20%, and 1 sample had a crack or loss of 100% after the 3rd cycle. For all samples, crushing under the fingers was observed, along with mass and strength loss indicators, and it was concluded that miljevina is unstable in saturated sodium sulfate solution.



Figures 18-19. Tenelija and miljevina samples after the  $2<sup>nd</sup>$  cycle (left) and  $5<sup>th</sup>$  cycle (right) of testing with sodium sulfate solution (IGH-MOSTAR, 2002) [26]

Table 7 shows the results of frost resistance test of (new) miljevina in saturated sodium sulfate solution.



Table 7. Frost resistance test of (new) miljevina in saturated sodium sulfate solution

• tests according to BAS EN 12371 with 14 freezing cycles on 15 test samples (10 K) 50 and 5 P 40x40x160 mm):

- in IGH Mostar (2016), it was determined by visual assessment that the samples did not show any changes in terms of peeling, crumbling and cracking. The solid structure of the samples remained unchanged, without a change in the apparent volume of the test samples, which leads to the conclusion that miljevina is resistant to the action of frost.

### **6. TESTING OF (NEW) MILJEVINA SAMPLES, WITH SPECIAL REFERENCE TO ITS FROST RESISTANCE**

As part of preparation of Milica Rončević's graduation thesis, the first step was a visit to the Revigrad company and the Mukoša deposit, during which various layers were examined, especially the tenelija intercalations within the miljevina beds. In addition to the analysis of available literature and test reports, the visit to the quarry was important for planning the research within this graduation thesis (Figure 20).



Figure 20. Visit to the Mukoša deposit near Mostar at the beginning of development of the graduation thesis [27]

Samples of miljevina, namely of colorful miljevina and white miljevina, as two types of miljevina with different properties, which were not recognized as such during previous tests, were collected for testing during the visit. Colorful miljevina is characterized by colorful patterns and inhomogeneous texture, as a result of different mineral inclusions and variations in sedimentation processes. It consists of several minerals and often has a colorful or heterogeneous texture, where different minerals can result in variations in compressive strength. In contrast, white miljevina is characterized by its uniform, light color and homogeneously fine structure, which makes it suitable for specific aesthetic and functional applications. It contains a higher concentration of certain minerals or has a more homogeneous structure in relation to the more colorful variant, which contributes to a higher average compressive strength, because a more homogeneous structure is usually more mechanically resistant. After identification and classification, samples of both types of miljevina were carefully sawn into cubes with an edge of 5 cm in the stonemason's workshop Maslina in Čitluk in order to test its physical and mechanical properties, which was performed in the accredited Central Laboratory of IGH d.o.o Mostar. The received samples with laboratory marks 24/367 for white miljevina and 24/368 for colorful miljevina were visually inspected, and their edges

were blunted to make sure that they were in an appropriate condition for testing. It was important to ensure that the samples were not physically damaged and did not contain visible impurities.



Figures 21-22. Blunted edges of samples of white miljevina (left) and colorful miljevina (right) [27]



Figure 23. Measuring the dimensions of test samples in the Central Laboratory of IGH d.o.o. Mostar [27]

## **6.1. Simplified petrographic description (macroscopic and microscopic determination)**

Mineralogical-petrographic analysis of white miljevina and colorful miljevina was carried out at the Faculty of Mining, Geology and Civil Engineering, University of Tuzla in 2024 [28] and the following results were obtained.

Macroscopic determination: The color of the rock is beige in the dry state, and changes to brown with the action of water. It disintegrates easily. The fracture surfaces are uneven and rough. The fracture edges are moderately sharp. No cracks were observed in the rock. Irregular openings - pores, with a diameter of up to 0.3 mm, on average 0.07-0.15 mm, were observed on the exterior of the rock and on fracture surfaces. The reaction to diluted HCl acid

is violent and instantaneous with rapid absorption of the acid into the rock. The insoluble residue (after the action of HCl acid) is negligible. No fossil remains or opaque minerals were observed in the rock.

Microscopic determination: The base of the rock is made of cryptocrystalline calcite micrite (up to 15 µm), the primary fine-grained component of carbonate sediments. Micrite appears as a dense, muddy mass. Such a grain diameter determines the uniformity in terms of mineral composition and structural-textural characteristics. Pore spaces, up to 0.3 mm in size, were detected in the rock. The occurrence of microsparite as a result of the recrystallization of micrite into sparry calcite was detected around the boundaries of the pore spaces. The diameter of sparry calcite grains ranges from 0.10 to 0.20 mm, with an average of 0.15 mm. According to the classification of Compton (1962), the rock belongs to limestones  $(96.81\%$  CaCO<sub>3</sub>).



Figure 24. Classification of rocks according to Compton

**Texture**: Massive; **Structure**: Cryptocrystalline (dominant) to microcrystalline;

**Rock**: Sedimentary, cohesive, carbonate: limestone, micrite, moderately porous.



Figures 25-27. Mineralogical-petrographic analysis of the sample of white miljevina, mark 24/367 [28]

Macroscopic determination: The color of the rock is beige in the dry state, and changes to brown with the action of water. It disintegrates easily. The fracture surfaces are uneven and rough. The fracture edges are moderately sharp. No cracks were observed in the rock. Irregular openings - pores, with a diameter of up to 1.2 mm, on average 0.4-0.7 mm, were observed on the exterior of the rock and on fracture surfaces. The reaction to diluted HCl acid is violent and instantaneous with rapid absorption of the acid into the rock. The insoluble residue (after the action of HCl acid) is negligible. No fossil remains or opaque minerals were observed in the rock.

Microscopic determination: The main petrogenic mineral is calcite, which occurs in the rock as micrite (over 95%). Micrite represents the primary compositional element of the rock mechanically deposited as carbonate sediment after longer or shorter water transport. Such a grain diameter determines the uniformity in terms of mineral composition and structural-textural characteristics. Pore spaces, with dimensions up to 1.2 mm, most often 0.4-0.7 mm, were detected in the rock. At the base of the rock, but also around the boundaries of the pore spaces, the occurrence of microsparite was detected as a result of the recrystallization of micrite into sparry calcite. The diameter of sparry calcite grains ranges from 0.20 to 0.40 mm, on average 0.25 mm. According to the classification of Compton (1962), the rock belongs to limestones  $(93.82\% \text{ CaCO}_3).$ 

**Texture**: Massive.

**Structure**: Cryptocrystalline (dominant) to microcrystalline.

**Rock**: Sedimentary, cohesive, carbonate: limestone, micrite, porous.



Figures 28-30. Mineralogical-petrographic analysis of the sample of colorful miljevina, mark 24/368 [28]

The analyzed samples of white miljevina and colorful miljevina, marks 24/367 and 24/368, belong to sedimentary, cohesive carbonate limestone rocks. Considering their structural characteristics, they are defined as micrites (the rock base consists of micrites in the amount

of over 95%), and considering the frequency of pores, they are also characterized as porous. Pores, which are larger and more common in sample 24/368, are detected in both samples. The micrite structural type indicates the depositional environment - a shallow lacustrine environment without turbulent movements. Fossil remains and opaque minerals were not found in the samples.

## **6.2. Chemical analysis**

Chemical analysis of white miljevina and colorful miljevina was conducted at the Faculty of Mining, Geology and Civil Engineering, University of Tuzla in 2024, and the results are presented in Table 8 and Table 9 [28].





*Note: The content of CaCO3 obtained by stoichiometry is 96.81%.* 

#### Table 9. Chemical composition of colorful miljevina, mark 24/368 [28]



*Note: The content of CaCO3 obtained by stoichiometry is 93.82%.* 

The chemical composition indicates limestones with a high percentage of  $CaCO<sub>3</sub>$  (93.82%) - 96.81%) and a low content of harmful components.

#### **6.3. Physical-mechanical tests**

After careful examination, the mass and dimensions of the dried test samples were precisely determined and they were marked with appropriate numbers. Besides, Table 10 shows a comparison of test results of samples of "(new) miljevina" from the Mukoša quarry.

Table 10. Comparison of test results of samples of "(new) miljevina" from the Mukoša quarry [27]





Analyzing the obtained results of the tested varieties of colorful miljevina, it can be concluded that the obtained mean value of bulk density is 1.764 g/cm<sup>3</sup>, which is quite below the lower limit of the interval of the obtained results of the miljevina tests in the period 1998-2016 (1.805- 1.836 g/cm<sup>3</sup>), but very close to the result obtained by the 2017 test at the Faculty of Civil Engineering University of Sarajevo (FCE UNSA) of 1.759 g/cm $^3$ , which has been an exception in relation to other results for years. On the other hand, the obtained mean value of the bulk density of white milievina of 1.919  $q/cm<sup>3</sup>$  significantly exceeds the upper limit of the specified interval of the previous results of miljevina and is at the lower limit of the previously obtained results of the tenelija tests (1.920-2.018 g/cm<sup>3</sup>). The results were obtained on a large number of tested samples, with a small scatter, especially for white miljevina. According to the results of the bulk density tests, it could be said that colorful miljevina is among the worst tested miljevinas, and white miljevina is among the best. The earlier interval of the obtained test results of the bulk density of miljevina can be extended to 1.759-1.919 g/cm $^3\!$ .

 Testing the open porosity of colorful miljevina, the mean value of 27.5% was obtained, which is a poor result that is outside the interval of previously obtained results (26.5-27.0%), while the obtained mean value of the open porosity of white miljevina was 25.8%, which is a better value compared to the specified interval of previous results. The results were obtained on a large number of tested samples, with a small scatter, especially for white miljevina. According to the open porosity test results, it can be said that colorful miljevina belongs to the worst tested miljevinas, and white miljevina to the best miljevinas. The previous interval of the obtained test results of the open porosity of miljevina can be extended to 25.8-27.5%.

 By testing the water absorption of the colorful miljevina, the mean water absorption value of 15.6% was obtained, with a minimum value of 13.1% and a maximum value of 18.3%. The coefficient of variation of 9.3% indicates a slightly higher variability of the results. On the other hand, white miljevina shows a lower mean water absorption value of 13.4%, with a minimum value of 12.4% and a maximum value of 14.7%. The coefficient of variation of 4.6% suggests a lower variability and homogeneous structure of the stone. These results indicate that white miljevina is more consistent in terms of water absorption compared to colorful miljevina. The previous interval of the obtained absorption results of miljevina (14.10-16.24%) can be extended to 12.7-18.3%.

As for the analysis of the mean results of the compressive strength tests, they were obtained on a relatively large number of samples, with a large scatter of the compressive strength tests results, which is typical of stone as a building material. This is understandable because stone is a material that is formed in nature in very complex and variable climatic, geological, ecological and other conditions, over long periods of time in millions of years. In practice, when testing the tensile and compressive strength of stone, the coefficient of variation is taken in the interval from 8 to 20%. The diversity of the results is visible from the value of the coefficient of variation, as the ratio of standard deviation to arithmetic mean of the test results. Therefore, the limit value of the coefficient of variation was taken as 20%, and in further analysis of test results, the part of the results that deviated the most was discarded, while calculating a new mean value, standard deviation and coefficient of variation.

The mean value of the compressive strength in dry state on 21 samples of white miljevina was 21.9 MPa, with a high coefficient of variability of 29.3%. After discarding the results that deviated significantly (marked in red in Table 8), a new mean value of the compressive strength in dry state of 23.0 MPa (coefficient of variation 11.7%) was obtained from the remaining 14 results, which is at the upper limit of the interval of previously obtained results (18.3-23.3 MPa).

In the case of colorful miljevina, after discarding variable results, the mean value of the compressive strength in dry state was 12.8 MPa, which is far below the specified interval of results, even below the result obtained in the 2017 test at FCE UNSA of 15.1 MPa, which was an exception compared to the other results and was left out of that interval.

 Therefore, the interval of the obtained test results of the compressive strength in dry state can be expanded to 12.8-23.3 MPa, with the interval of individual results being even much wider, from only 6.3 to as much as 31.1 MPa.

 The mean values of compressive strengths in water-saturated state are below the interval of previously obtained results, both for white miljevina (14.3 MPa), and especially for colorful miljevina of 7.7 MPa, which is somewhat lower than the result obtained in 2017 at FCE UNSA of 8.3 MPa, which was an exception compared to the other results, that is, from 13.84-17.0 MPa. The interval of previously obtained compressive strength test results in water-saturated state is expanded to (7.7)/13.84-17.0 MPa, with an even wider interval of individual results, from only 3.8 MPa to 24.0 MPa.

For white miljevina, with significant variations in results, the mean compressive strength after 25 cycles of frost testing was as much as 21.7 MPa, which is slightly less than the strength in dry state (23.0 MPa) and significantly higher than in water-saturated state (14.3 MPa). The results were obtained on a large number of samples, with some results being discarded due to large scatter. Most samples showed minimum mass changes and rare damage such as peeling, crumbling and cracking. Mass changes are minimal for most samples, which indicates a relatively stable state of the material after exposure to testing. The highest mass change was registered for sample number 22, with a change of 4.09%, while other mass changes ranged from 0.08% to 0.49%.

For colorful miljevina, with significant variations in results, the mean compressive strength after 25 cycles of frost testing was 12.0 MPa, which is slightly lower than the strength in dry state (12.8 MPa) and significantly higher than in water-saturated state (7.7 MPa). The results were obtained on a large number of samples, with some results being discarded due to large scatter. The reasons why the compressive strength after a cycle of frost is higher than the strengths in dry and water-saturated states may be different, excluding reasons related to the laboratory, which is accredited, the press is calibrated, the testers are trained, and the temperatures are ensured. A possible influence on the results is that the samples that were exposed to frost were more compact or less porous compared to the samples that were tested in the dry and water-saturated states.

#### **6.4. Frost resistance testing**

 For both varieties of miljevina, frost resistance testing was conducted using three methods, two of which were crystallization, with magnesium sulfate (BAS EN 1367-2) and sodium sulfate (JUS B.B8.002 standard), and after 25 freezing and thawing cycles (JUS B.B8.001 standard) (Figures 31-32.).



Figures 31-32. View of tested samples of colorful miljevina, mark 24/368, destroyed by magnesium sulfate (left) and sodium sulfate (right) [27]

#### 6.4.1. Frost resistance testing of colorful miljevina

The frost resistance in a magnesium sulfate ( $MqSO<sub>4</sub>$ ) solution was tested using the BAS EN 1367-2 standard: "Tests for thermal and weathering properties of aggregates - Part 2: Magnesium sulfate test", which is primarily used to assess the resistance of aggregates to degradation caused by magnesium sulfate ( $MqSO<sub>4</sub>$ ). After testing, the following characteristics of the degradation of colorful miljevina were observed:

Loss of shape: Most of the stone samples have lost their original cube shape. The edges are visibly rounded, and many samples no longer look like regular cubes. This indicates significant material wear and erosion of the edges and surfaces due to the wetting and drying cycles in the  $MdSO<sub>4</sub>$  solution.

Reduction in dimensions: The dimensions of the samples are visibly reduced, which means that a significant part of the material has eroded or fallen off during the test. The pieces are smaller than would be expected for cubes with edge of 5 cm, which confirms degradation.

Cracks and breaks: The surface of some samples shows cracks and breaks, which is a sign of physical damage. Small pieces of stone that have separated from the main samples can be observed, further indicating their brittleness after exposure to the  $MqSO<sub>4</sub>$  solution.

Change in texture and color: The texture of the stone appears rougher and less compact than before testing, which may be the result of salt crystallization within the pores of the stone and their expansion during the cycle. A change in the color of the stone can be observed due to the chemical reaction between the sulfate and the mineral composition of the stone.

Thus, the samples of colorful miljevina (24/368) showed great degradation, which is evident from significantly more damaged and deformed pieces. Based on the test results, it can be concluded that the colorful miljevina has significantly degraded after exposure to magnesium sulfate. Loss of shape, reduction in dimensions, presence of cracks and general material wear clearly indicate the high sensitivity of this stone to chemical and physical erosion caused by cycles of wetting and drying in the  $MdSO<sub>4</sub>$  solution.

To test the resistance to frost in a sodium sulfate (NaSO4) solution, the JUS B.B8.002 standard was used, and it was applied to the white miljevina and colorful miljevina stones in the research within this graduation thesis.

After testing, the following characteristics of the degradation of colorful miljevina were observed:

Surface degradation: White deposits of salt are visible on the surface of the samples, which indicates the crystallization of sodium sulfate within the pores of the stone. The surface of the samples is coarse and rough, which suggests significant damage and erosion of the material.

Physical damage: Several samples show severe cracks and breaks. Parts of the samples have separated, which indicates a high degree of degradation. Some samples have broken into smaller pieces, which is a sign that the internal structures of the stone were under great stress due to salt crystallization.

Reduction in size and shape: Samples no longer have a regular cube shape. The edges are considerably damaged, and the dimensions of the samples are reduced due to erosion. Changes in shape and volume clearly indicate that the material has lost a significant part of its mass.

Presence of cracks and delamination: Cracks and layers of material that have delaminated are visible, which is typical of a stone subjected to cyclic freezing and thawing in the presence of salt. This delamination indicates weaknesses in the stone structure that are exacerbated by the action of salt crystallization.

Based on the visual inspection of the samples, the samples of colorful miljevina, mark 24/368, showed a high degree of degradation, with serious damage, cracks and delamination.

By testing with 25 freeze-thaw cycles according to the JUS B.B8.001 standard, the effect of freezing and thawing on the stone was simulated in order to assess its resistance to cyclical temperature changes that can cause physical damage. The standard is especially useful for assessing materials that will be exposed to extreme weather conditions. Before and after completing all cycles, the samples were weighed to determine the mass loss, which is expressed as a percentage of the initial mass of the sample. The samples were inspected for physical damage such as cracks, breaks or other types of degradation.



Figures 33-35. View of the colorful miljevina samples, mark 24/368, used during the testing with 25 cycles (left); view of the damaged edges of the samples after testing the samples with mark 24/368-25 (middle) and 24/368-32 (right) [27]

All results, including measurements of mass loss, changes in volume, density, and visual observations of the samples of colorful miljevina, mark 24/368, were documented and analyzed. Changes in the mass of the samples before and after the test with 25 cycles of freezing/thawing on 17 undamaged samples out of a total of 21 samples were minimal and were 0.00-0.19%. Peeling, crumbling and cracking were observed on 4 samples, with changes in mass of 0.09%, 0.18%, 1.48% and 4.38%. Based on the test results, a conclusion was made on the resistance of colorful miljevina to cyclic freezing and thawing and its suitability for use in conditions where it will be exposed to frost.

#### 6.4.2. Testing the frost resistance of white miljevina

Samples of white miljevina also showed degradation, which is evident from considerably more damaged and deformed pieces, but less compared to colorful miljevina. (Figures 36-37.)



Figures 36-37. View of the tested samples of white miljevina, mark 24/367, destroyed by magnesium sulfate (left) and sodium sulfate (right) [27]

Twenty samples of white miljevina, mark 24/367, showed better resistance, but from the figure it is evident that these samples were also significantly degraded, but slightly less than colorful miljevina. The changes in the mass of the samples before and after testing for 25 freeze/thaw cycles on 15 undamaged samples out of a total of 20 samples were minimal and amounted to 0.08-0.32%. Peeling, crumbling and cracking were observed on 5 samples, with changes in mass of 0.21%, 0.25%, 0.41%, 0.49% and 4.09%.

## **6. CONCLUSIONS**

Freshwater limestone Mostar miljevina or miljevina for short, together with the higher quality tenelija, is intercalated in the Mukoša deposit near Mostar. Although slightly degraded by cracks and fissures, they are quite compact, strong and tough, and represent a good raw material for the production of dimension stone, so they have been used in construction since ancient times. Miljevina has a dense, submicroscopic fine-grained structure in which there are few or no ooids, in which the cementation and recrystallization of calcite (dense limestone) have not taken place. For this reason, it retains moisture for a long time, and the effect of temperature changes and ice causes surface loosening and deterioration of the stone. In old buildings with walls made of miljevina, the problem of increased moisture has always occurred, so they were protected with facades, with the use of another type of stone in the lower part of the building that is in contact with the ground (for foundations and basement), which is part of the construction tradition, the reason for which is the high absorption of miljevina.

In the conditions of modern use of miljevina for facade cladding and as a decorative stone, the above-mentioned relations to wetting and moisture are markedly unfavorable, which is why stone cladding is protected with a highly water-repellent impregnating agent.

The variety of freshwater limestone colorful miljevina consists of several different minerals and often has a colorful or heterogeneous texture, where different minerals can have different mechanical properties, which can result in variations in compressive strength. Based on all the test results, it is evident that it is a variety of miljevina of poor quality, because the obtained property test results are at the lower limit, or below the lower limit of the interval of the results obtained so far.

The variety of freshwater limestone white miljevina contains a higher concentration of certain minerals or has a more homogeneous structure in relation to the colorful miljevina, which contributes to a higher average compressive strength, because a more homogeneous structure is usually more mechanically resistant. Based on all the test results, it is evident that it is a variety of miljevina of very good quality, because the obtained property test results are above the limit of the interval of the results obtained so far, except for the compressive strength results. The test results obtained as part of the graduation thesis expanded the range of existing test results of miljevina, or the interval of all available test results.

Regarding the frost resistance test of freshwater limestones, including miljevina, it is evident that crystallization tests are not suitable for use with this type of stone, and that the method of cyclic freezing and thawing with 25 cycles, with minimum changes in the mass of the samples, proved to be much better. In this sense, on the remaining samples it is proposed to perform an additional frost resistance test according to BAS EN 12371 with 14 test cycles, which will probably prove to be the optimal of all 4 test methods for freshwater limestones, including miljevina.

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