ZEOLITES-SUSTAINABLE BUILDING MATERIAL

Todorka Samardzioska
Ss. Cyril and Methodius University

Milorad Jovanovski
Ss. Cyril and Methodius University

ZEOLITES - SUSTAINABLE BUILDING MATERIAL

Todorka Samardzioska[1], Milorad Jovanovski[1], Sonja Lepitkova[2]

[1] Ss Cyril and Methodius University, Faculty of Civil Engineering, blvd Partizanski odredi 24, 1000 Skopje, Macedonia, email: samardzioska@gf.ukim.edu.mk, jovanovski@gf.ukim.edu.mk

[2] University of Goce Delcev in Shtip, Faculty of Natural and Technical Sciences, Krste Misirkov No.10-A, 2000 Shtip, Macedonia, email: sonja.lepitkova@ugd.edu.mk

SUMMARY: Zeolites are natural porous volcanic tuffs that represent hydrated crystalline aluminosilicates minerals with alkaline and earth-alkaline metals. Their chemical properties, a large percentage of porosity, ability of adsorption of the material define high specific surface and low specific weight. Many experimental studies confirm zeolites' excellent mechanical properties that include this material in the group of building materials for structural elements. Another use of zeolite is as an additive in cement, as an active mineral supplement and binder component for silicate concrete and as gypsum cement pozzolatic binder component and concretes based on them. A mixture of cement and zeolite is used for the production of high-strength concrete with greater compression resistance than that of Portland cement. Primary objective of this paper is to investigate the field of application of zeolites found near Probishtip in Macedonia. Properties of the individual zeolites strongly depend on the location of the site. Therefore, experimental testing has been performed in order to define mechanical properties of the local zeolites. Water absorption, porosity, specific weight and mechanical properties have been determined. Additional testing of the physical and mechanical properties of the zeolites can open new horizons in the industry of building materials in Macedonia. This newly discovered material is feasible, easily mined from quarries and easily processed. It contributes to greener and safer environment in many ways or plays a significant role in reducing toxic waste and energy consumption. In fact, almost each application of zeolites has been introduced because of environmental concerns. The results of the parameters obtained from laboratory tests will provide guidance on opportunities for the proper application of local zeolite, in terms of both natural stone and as filler for obtaining a light mortars and concretes.

ZEOLITI – ODRŽIVI GRAĐEVNI MATERIJALI

SAŽETAK: Zeoliti su prirodni porozni vulkanski tufovi sastavljeni od hidratiziranih kristaliničnih alumosilikatnih minerala s alkalnim i zemnoalkalnim metalima (engl. alkaline earth metals). Njihova kemijska svojstva, velik postotak poroznosti i sposobnost adsorpcije materijala određuju veliku specifičnu ploštinu, a malu specifičnu težinu. Mnoge eksperimentalne studije potvrđuju izvanredna mehanička svojstva zeolita koja taj materijal svrstavaju u skupinu građevnih materijala za konstrukcijske elemente. Druga je upotreba zeolita kao dodatka u cementu, kao aktivnog mineralnog dodatka i vezivne komponente za silikatni beton i kao pucolanske komponente veziva cementa s gipsom i betona izrađenih s takvim sastojcima. Za proizvodnju betona s većom tlačnom čvrstoćom od betona s portlandskim cementom upotrijebljena je mješavina cementa i zeolita. Glavni cilj ovog rada bio je istražiti mogućnost primjene zeolita iz nalazišta kraj Probištipa u Makedoniji. Svojstva pojedinih zeolita znatno ovise o lokaciji. Stoga su provedena ispitivanja radi definiranja mehaničkih svojstava lokalnih zeolita. Određeni su vodoupojnost, poroznost, specifična težina i mehanička svojstva. Dodatna ispitivanja fizičkih i mehaničkih svojstava zeolita mogu otvoriti nove vidike industriji građevnih materijala u Makedoniji. Taj novootkriveni materijal je prikladan, lako se vadi u nalazištu i lagano prerađuje. On doprinosi zelenijem i sigurnijem okolišu na više načina i ima značajnu ulogu u smanjenju otrovnoga otpada i potrošnji energije. S obzirom na okolišne aspekte moguća je gotovo svaka primjena zeolita. Rezultati parametara dobivenih laboratorijskim ispitivanjima smjernica su za mogućnosti odgovarajuće primjene lokalnoga zeolita kako kao prirodnog kamena tako i kao ispunskog materijala za dobivanje laganih mortova i betona.

1. INTRODUCTION

Zeolites are natural porous volcanic tuff with high adsorptive ability, high specific surface and low specific weight, which, by their chemical structure, represent hydrated alumina-silicate structured minerals that contain alkaline and earth-alkaline metals.

As a material, the zeolites are characterized with a high open porosity. Throughout their endless three-dimensional crystal structure, the zeolites have uniformly sized pores, called windows, which is actually an effective open porosity directly connected to the open specific surface, i.e. the surface in the interface of the material with the surrounding medium.

All naturally occurring zeolites are hydrophilic (having affinity for polar molecules, such as water). Therefore, they can act as adsorbers, adsorbing the contaminants and pollutants in their surface.

Due to their ability for water adsorption, exchange of cations, dehydration - rehydration, zeolites are considered as the environmentally cleanest materials and they are widely used in agriculture, medicine, construction and environmental protection, especially for treatment of urban wastewater and decontamination of radioactive waste water. The natural zeolites can remove different heavy metals from drinking water and therefore they are widely used as a suitable technical and economic solution for water treatment. Also, zeolites they can be used for commercially successful applications to separations of mixtures, especially for supercritical or close-boiling liquid mixtures that are poor candidates for separation by distillation.

The use of zeolite in construction dates back a long time ago, primarily due to its excellent mechanical properties, Chmielevska, [1]. Namely, its absorption of water, porosity, specific weight and mechanical properties are parameters that impose application of the zeolite in constructions. There are a number of studies in the world, related to the mechanical properties of volcanic tuffs pertaining to its use in construction, Hudymaa at al., [2], Marcari at al., [3] as a foundation basis, Price, [4] or as masonry blocks in buildings, Marcari, [5].

Furthermore, this research shows that characteristics of individual zeolites depend on the location of the site itself. The tests made on samples of tuff from multiple sites in Turkey in terms of the compressive strength, abrasion, porosity, water absorption and density, recognize the zeolite as a material with high porosity, large capacity of water absorption and high compressive strength, whose characteristics change depending on the site, Yasar et al., [6]. Comparison of mechanical properties of zeolite tuff in Çanakkkale, Turkey, used to build the Temple of Apollo and the tuff situated in close proximity, Ergenç, [7], confirmed its excellent properties as a building stone.

Exploitation of zeolite in Republic of Macedonia was carried out for the first time in 2013 at the site Slavishko Pole near the village of Vetunica, from "Strmosh AD" – Mines for non-metals. In order to start application of this type of zeolite, and starting from the fact that the properties of the individual zeolites depend on the location of the site [7], it is necessary to do extensive research on defining its characteristics and properties.

This paper represents the experimental tests for determination of the mechanical properties of natural zeolite obtained from the Strmosh Mine. The procedure of examination performed on two series of cubes of zeolite is illustrated, in dry condition and in saturated condition. As a result of the procedure, the compressive strength and the ability of water absorption of the material have been determined.

2. EXPERIMENTAL METHODS

The experimental testing for determination of the mechanical properties of the zeolites has been performed in the geotechnical laboratory at the Faculty of Civil Engineering in Skopje. The testing was conceptualized in two parts: determination of the percentage of water absorption and determination of the compressive strength. The compressive strength, one of the essential mechanical properties of any material, was determined by specimens in dry condition and by specimens in saturated condition, in order to check the manner by which the water in the pores in the material affects the compressive strength. In order to obtain reliable results, the experimental testing was performed in accordance with the standards EN 13755:2008 [8] and EN 14617-15:2005 [9]. Specimens are with cubical shape, extracted from a zeolite block with larger dimensions, and all damaged and loose parts are removed from them, according to the standard EN 14617-15:2005 [9].

In order to get smooth and parallel surfaces for application of the compressive forces, they were flattened by gridding until traces of cutting were removed from the samples. The specimens, i.e. cubes, are with standardized dimensions of 50±1mm, Figure 1, and mass between 180 and 200 gr, depending on the sample, Table 1. The specimens tested in dry condition were marked with a mark M-S, while the specimens in saturated condition are marked with a mark M-W. Numbers 1, 2 and 3, after the mark, indicate the appropriate testing specimen.

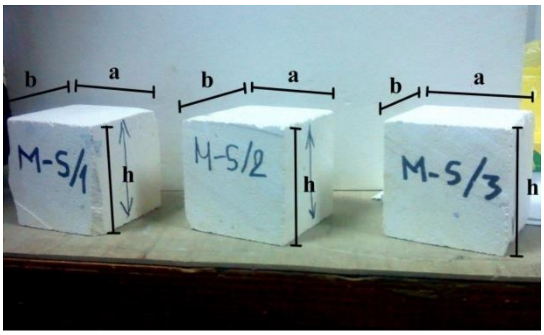

Figure 1: Geometrical characteristics of the specimens

Both series of the experimental specimens are firstly dried to temperature of 105°±5°C. Afterwards, they have been cooled and weighed on a scale with an accuracy of ± 0,01g. In that way, the mass of each specimen in dry condition was determined respectively, Table 1.

Table 1: Geometrical characteristics and mass of the specimens

Specimen	Dimensions			Mass in dry condition
	a	b	h	m_{dry}
	[cm]	[cm]	[cm]	[g]
M-S/1	5,17	5,18	5,16	185,41
M-S/2	5,16	5,20	5,13	189,42
M-S/3	5,17	5,18	5,16	191,91
M-W/1	5,16	5,17	5,18	188,54
M-W/2	5,20	5,16	5,15	193,34
M-W/3	5,18	5,18	5,16	189,16

The second series of specimens for determination of the compressive strength in saturated condition is used for determining the percentage of water absorption, also. The experimental testing for obtaining the percentage of water absorption of the zeolite is carried out according to the method of gradual immersion under atmospheric pressure. The testing was initiated by immersion of the test samples to ¼ of their height in a container with distilled water. The container is gradually filled with water up to ½ of the height of the specimens after 1 h and after 2 h to ¾ of the height of the specimens. The specimens are completely submerged in water after 22 hours. The specimens are accessed for weighing of their mass after 24 h from the initiation of immersion. Before each measurement, the samples are dried with a soft cloth, in order to prevent evaporation of the absorbed water, according to EN 13755: 2008. Weighing of the mass of each sample was repeated every 24 hours, until the sample has reached complete saturation, Table 2.

Table 2: Mass of the testing specimens in saturated condition

Specimens	Mass in saturated condition m_{sat} [g]
M-W1	232,48
M-W2	236,55
M-W3	232,69

The experimental testing of the compressive strength has been performed using testing machine type 102/3000 HK-4, with capacity of 3000 kN. The specimens were set in a way that the compressive force was applied perpendicular to the material layers. The compressive force was gradually increased by 0,5 MPa/sec, until failure of the specimen, when the force at failure F and respective stress were registered, Figure 2.

a) 

b) 

Figure 2: Experimental testing: a) machine for testing compression strength, b) specimen

3. RESULTS AND DISCUSSION

3.1. WATER ABSORPTION

For the first series of three test samples, the percentage of water absorption was determined before defining compressive strength in saturated condition. The obtained results of the experimental testing are presented in Table 3.

The results in the Table 3 lead to conclusion that the quantity of absorbed water in each of the tested specimens is almost same, having the average water absorption of 23%.

Table 3: Experimentally obtained results for percentage of water absorption

Specimens	Water absorption
	U [%]
M-W1	23,31
M-W2	22,35
M-W3	23,01
Average value	22,89

3.2. COMPRESSIVE STRENGTH

The second part of the experiment, determination of the compressive strength of the zeolite in dry and saturated condition, was conducted on six specimens in total, i.e. on two sets of three specimens.

Experimentally obtained results for the compressive strength of zeolite in dry condition are presented in Table 4, while the results for the compressive strength in saturated condition are presented in Table 5.

Table 4: Mechanical properties of zeolite cubes in dry condition due to compressive stresses

Specimen	Bulk mass	Force at failure	Compressive strength
	ϒ=ms/V (kg/m3)	F (kN)	σp (MPa)
M-S1	1341.72	76.18	28.5
M-S2	1376.12	114.60	43.0
M-S3	1388.76	128.03	47.9
Average values	1369.87	106.27	39.8

Table 5: Mechanical properties of zeolite cubes in saturated condition due to compressive stresses

Specimen	Force at failure	Compressive strength
	F (kN)	σp (MPa)
M-W1	63.29	23.7
M-W2	90.87	33.9
M-W3	107.39	40.1
Average values	87.18	32.6

According to the standard EN 14617-15:2005, [9], the compressive strength of the zeolite is determined as an average of the compressive strengths of all three test specimens. In this case, the compressive strength of the zeolite cubes in dry condition is almost 40 MPa. From the conducted experimental testing, it can be concluded that the compressive strength of the tested specimens ranged from 28,5 MPa to 47,9 MPa.

As it was expected, the results shown in Table 5 of the tested specimens in saturated condition are lower than the results obtained from the experimental testing of the specimens in dry condition, presented in Table 4. Although the material is very porous and absorbs a large amount of water up to 23%, Table 3, the average compressive strength in saturated condition is 33 MPa. Comparing the results presented in Table 4 and Table 5, it can be concluded that the compressive strength of the zeolite decreases by 22% when the material is saturated with water.

The shape of fracture of the samples depends on the size of the friction that occurs at the interface between the sample and the plates through which the axial compressive force is applied. Inner friction prevents transverse deformation of the specimen and additional shear occurs, causing fracture in inclined planes, Figure 3a. This type of fracture is registered in four of the tested specimens. Practically, the compression testing system rather develops a complex system of stresses due to the end restraints by steel plates of the testing machine. Namely, due to the Poisson's effect, these four specimens undergo lateral expansion. However, the zeolite and the steel plates have different lateral expansions and as a result, tangential forces are induced at the contact between the zeolite cube and the steel plates of the machine. Therefore, as an addition to the compressive stresses, additional shear stresses are active in the zeolite specimen. The effect of the shear stresses decreases towards the centre of the cube, and the cracks at the centre are nearly vertical.

Fracture in the remaining two samples occurs in vertical planes parallel to the sides and approximately parallel to the applied load, Figure 3b. This type of fracture is registered in samples M-S/1 and M-W/1. The influence of shear stresses in these two specimens was smaller and they may failed by lateral splitting. They exhibit much lower compressive strength than the first four samples, both for dry and saturated condition. The compressive strength for these two samples is lower about 60% than the compressive strength of the first four samples, Table 4 and Table 5.

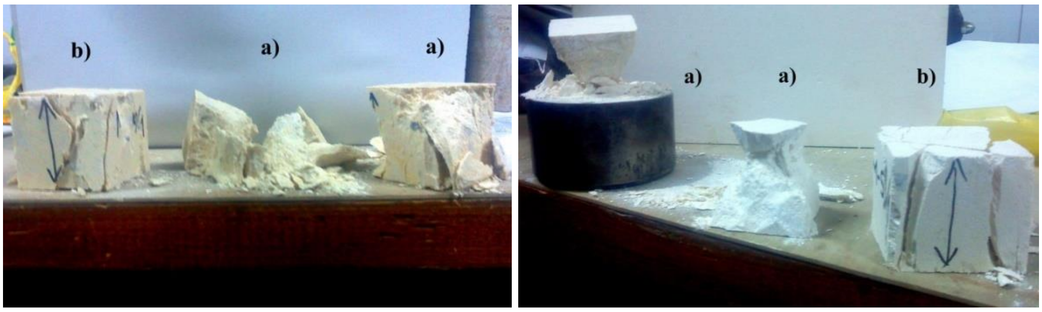

Figure 3: Type of failure in the tested specimens: a) failure in inclined planes, б) failure in planes parallel to the surfaces

The obtained results of the tests show a high value of compression strength of the material. From the comparison of the compression strength on both test series, it can be concluded that the series of samples in saturated condition have lower strength. This is due to the high porosity of the material that is accompanied by a large percentage of water absorption, which reduces the bearing capacity of the material.

4. CONCLUSIONS

The experimental research of two series of specimens of natural zeolite has been presented in this paper. The obtained results for the strength characteristics of the zeolite in dry and saturated condition, as well as its ability for water absorption, are main parameters for definition of its properties and suitable use.

This emphasizes the justification for application of this type of zeolite in structures. The obtained results of the tests show a high value of compressive strength of the material. As a result of the high porosity of the material, followed by a rate of water absorption, the compressive strength of samples in series in saturated condition is lower than the compressive strength of samples in dry condition.

Presented results lead to conclusion that the type of failure plays a major role in the compressive strength of the material. In the two specimens fractured in vertical planes parallel to the sides of the cubes, the compressive strength is much lower than in the specimens with inclined cracks. They exhibit much lower compressive strength than the first four samples, both for dry and saturated condition.

However, the results indicate a possible use of the zeolites not only in dry conditions, but also in conditions where the humidity is very high. Additional testing of the physical and mechanical properties of the zeolites can open new horizons in the industry of building materials in Macedonia. This newly discovered material in Eastern Macedonia is feasible, easily mined from quarries and easily processed. It contributes to greener and safer environment in many ways and plays a significant role in reducing toxic waste and energy consumption. In fact, almost each application of zeolites has been introduced because of environmental concerns. The results of the parameters obtained from laboratory tests will provide guidance on opportunities for the proper application of local zeolite, both, as a natural stone and as an agreggate for obtaining light mortars and concretes.

ACKNOWLEDGMENTS

The authors would like to express their gratitude to the members of the measurement team in the Laboratory of Geotechnics, at the Faculty of Civil Engineering in Skopje.

REFERENCES

[1] Chmielevska, E.: Zeolites – Materials of sustainable significance (short retrospective and outlook), *Environment Protection Engineering*, vol.36, No.4, pp. 129-135, (2010)

[2] Hudymaa, N.; Avarb, B.B. & Karakouzian, M.: Compressive strength and failure modes of lithophysae-rich Topopah Spring Tuff specimens and analog models containing cavities, *Engineering Geology* No. 73, pp. 179–190, (2004)

[3] Marcari, G.; Fabbrocino, G. & Lourenço, P.B.: Mechanical properties of tuff and calcarenite stone masonry panels under compression, 8th International Masonry Conference in Dresden, pp. 1083-1092, (2010)

[4] Price, R.H.: Analysis of Rock Mechanics Properties of Volcanic Tuff Units from Yucca Mountain, Nevada Test Site, Sandia National Laboratories, Albuquerque, (1983)

[5] Marcari, G.; Fabbrocino, G. & Lourenço, P.B.: Investigation on compressive behaviour of tuff masonry panels, University of Minho, (2010)

[6] Ergenç, D.: Investigation of tuff quarries around the Tample of Apollon Smitheus (Çanakkale, Turkey), Middle East Technical University, (2011)

[7] Yasar, E.; Tolgay, A. & Teymen, A.: Industrial Usage of Nevsehir-Kayseri (Turkey) Tuff Stone, *World Applied Sciences Journal* Vol. 7 No.3, pp. 271-284, (2009)

[8] EN 13755:2008, Natural stone test methods - Determination of water absorption atmospheric pressure, CEN/TC 246 -Natural stones.

[9] EN 14617-15:2005, Agglomerated stone - Test methods - Part 15: Determination of compressive strength, CEN/TC 246 -Natural stones.