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FEATURES OF ZEOLITIC TUFFS USED IN BUILDING CONSTRUCTIONS

BY

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Abstract. The increased need to replace existing materials (ceramic bricks, steel, concrete) with low embodied energy materials and good thermal insulation properties has required the capitalization on local resources. The present paper analyses zeolitic volcanic tuffs from Macicas quarry (NW from Cluj-Napoca town) from the point of view of putting them into value as natural and ecological building materials. The samples were tested for their physical and mechanical properties. The following methods and techniques were used: X-ray diffractions (XRD), which highlighted the mineralogical composition of the volcanic tuff and especially the high level of the present zeolites (clinoptilolite – 63.72% and phillipsite – 11.05%); microscopical tests on thin sections, which allowed the noticing of the processes of alteration of the volcanic glass, feldspars, mica, quartz, and electronic microscopy (SEM) in order to identify the zeolite crystals inside the voids of the tuff samples (Clinoptilolite). The tests (density, porosity, thermal conductivity, compressive strength) and mainly the high zeolite content (over 70%) proved that the tuffs have properties comparable to those of other building materials.

Key words: zeolitic tuff; mineralogy; thermal stability; energy; clinoptilolit; philipsite.

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1. Introduction

The zeolitic tuff was used, under the form of large stone blocks, as a building material since ancient times. The Greeks colonies and ancient Romans made use of the tuff blocks for constructing dwelling houses or cult and tomb monuments (ex: the entire city of Naples it was built of neapolitan zeolitic tuff) (Mumpton, 1999).

Zeolitic tuffs are currently used in various areas, depending upon the physical and mechanical properties, the mineralogical structure, the chemical compositions and the content of zeolites they possess.

In Romania, volcanic tuffs are to be found in wide areas in the Northern, Western and South-Eastern part of the Transylvanian Basin (where they are met in a referential stratigraphic layer) as well as in intramountaineous areas (in Apuseni) and on the outer range of the Carpathian mountains (the Western Carpathians) (Fig. 1 *b*).

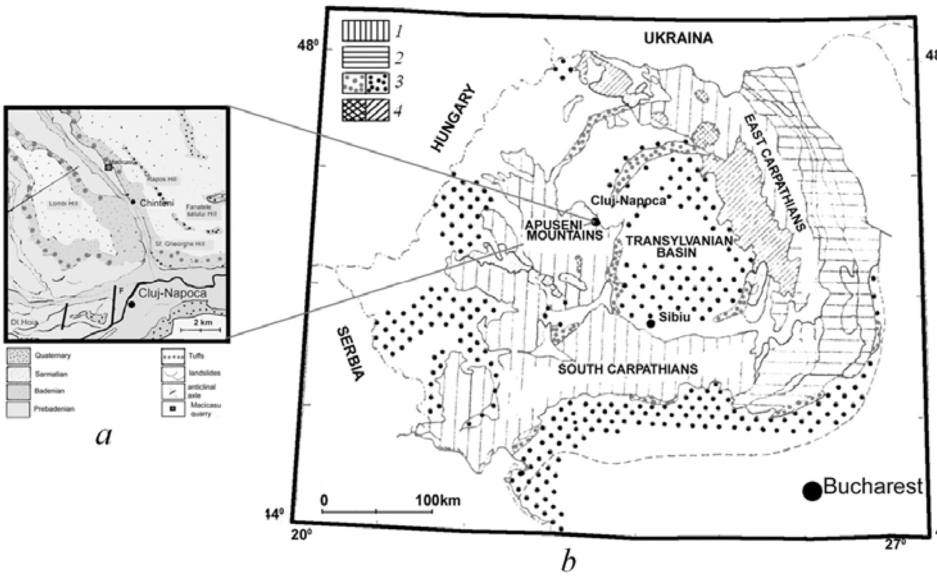


Fig 1 – *a* – the Badenian Tuffs from Cluj zone (Macicas quarry – NW of Cluj-Napoca town); *b* – *1*-Inner Carpathian Units; *2*-Outer Carpathian Units; *3*-Acid calc-alkaline volcanism: *a* – cropping out, *b* – burried; *4*-Intermediate cab-alkaline magmatism: *a* – intrusive, *b* – stratovolcanic (Seghedi *et al*., 2000, modified).

The age of the tuffs of the Transylvanian Basin dates back to the lower Miocene or Badenian (Lower Badenian); they are often related to the Dej Tuff Complexe.

The Dej Tuff Complexe, ”in all its occurrences, has a high zeolite content, as compared to the post-Badenian tuffs, which are also less extended and less often met”(Măicăneanu *et al*., 2008).

2. Mineralogical-Petrographical Properties

In Cluj area (Fig. 1 *a*), tuff crops belonging to the Dej Tuff Complexe, can be encountered in: Alunis, Apahida, Bobâlna, Chinteni, Corneşti, Cuzdrioara, *Macicaş*, Ocna Dejului, Paglişa, Şoimeni, Tioc.

For the purpose of our research, we used tuff excavated from the Macicas quarry. Its colour is white, greenish or green (the green one is rich in zeolites), massive, compact, faneritic, microgranular and isotropic.

The tuff has a basically vitreous mass (rich in volcanic glass with more or less zeolites in content), and bioclasts. When the volcanic glass is changed, in the basic mass, an almost amorphous mixture of chlorite, sericite, clay minerals, oxi-hydroxides of iron and zeolites (products of silicates, mainly of volcanic glass alteration) can occur.

The mineralogical composition was established by means of microscope-based tests (from thin sections using a Jenapol polarizing microscope), X-ray analysis (XRD) diffraction and SEM (scaning electron microscopy).

2.1. XRD Analysis

In order to identify the structure, the X-ray diffraction (Fig.2) technique with crystalline powders was used. The difractograms were recorded in a standard X-ray device, of type BRUKER D8 ADVANCE.

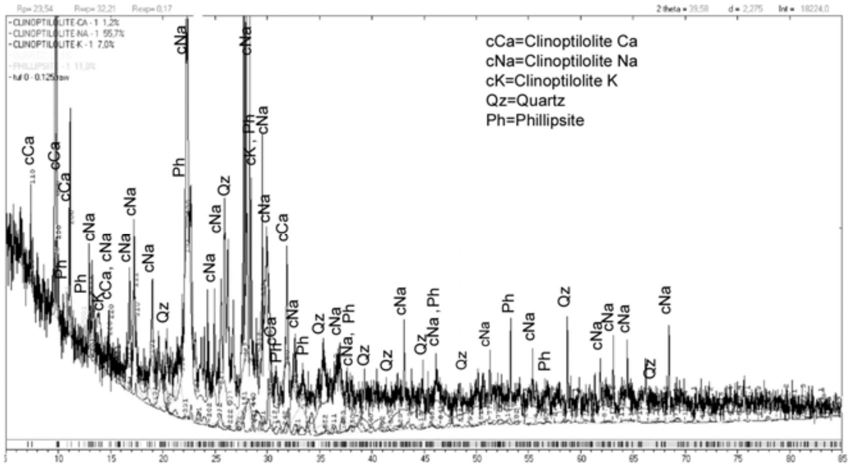


Fig. 2 – The Macicas tuff X-Ray diffraction.

The diffraction-related data were collected in angular steps of $\Delta 2\theta =$ $= 0.01$ degrees. It has been used the Cu K_{α} radiation with a Ni filter to remove the CuK_{β} and a Ge monocromator to remove $CuK_{\alpha 2}$. The XRD were recorded on BRUKER D8 Advance X-ray diffractometer, working at 45 kV and 45 mA. The CuK_{α} radiation, Ni filtered, was collimated with Soller slits. A germanium monochromator was used. The data of the X-ray diffraction patterns were collected in a step-scanning mode with steps of $\Delta 2\theta = 0.01°$. Pure silicon powder (standard sample) was used to correct the data for instrumental broadening. The experimental tests made use of the angular diffraction range of $2\theta = 5...85$ degrees.

The analysis of the X-ray diffraction result on a tuff sample (ground and sieved through a sieve of 0.125 mm) pointed out the major presence of a main mineral belonging to zeolites (aluminium-silicates hydrated with alkaline or alkaline-earth cations, of three dimensional crystalline structure), namely clinoptilolite (63.72%) accompanied by quartz (25.13%) and phillipsite (11.05%) (see Table 1).

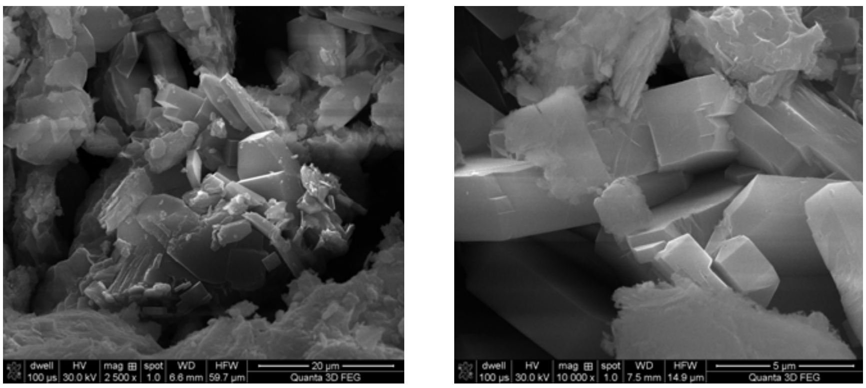
Table 1

The Mineralogical Composition Analysis of the Tuff (*the Grains Size 0...0.125 mm*)

Clinoptilolite-Ca % vol	Clinoptilolite-Na % vol	Clinoptilolite-K % vol	Quartz % vol	Phillipsite % vol
1.18	55.67	6.97	25.13	11.05

2.2. SEM Analysis

Electronic microscopy (SEM) helped the identification of prism-shaped crystals of clinoptilolite in the pores of the tuff under investigation, where the void walls were covered on the external side with volcanic glass (Fig. 3).



a *b*

Fig. 3 – Images to scaning electron microscopy (SEM) of zeolite:
a – clinoptilolite in the voids of the Macicas tuff; *b* – clinoptilolite-detail.

2.3. Thin Sections

Tuffs are mainly formed of glassy basic mass (zeolitised) in which primary minerals appear: quartz crystaloclasts (with magmatic absorbtion – Fig. 4 *a*) and plagioclase feldspar (in twins and continuous zonation, sometimes zeolitised – Fig. 4 *b*), biotite, zirconium, opaque minerals (probably hydro-thermal deposits) and secondary minerals, zeolites (clinoptilolite and philipsite) filling the voids.

Besides volcanic glass, zeolitization also affected the crystaloclasts of plagioclase (Fig. 4 *c*), micas and quartz.

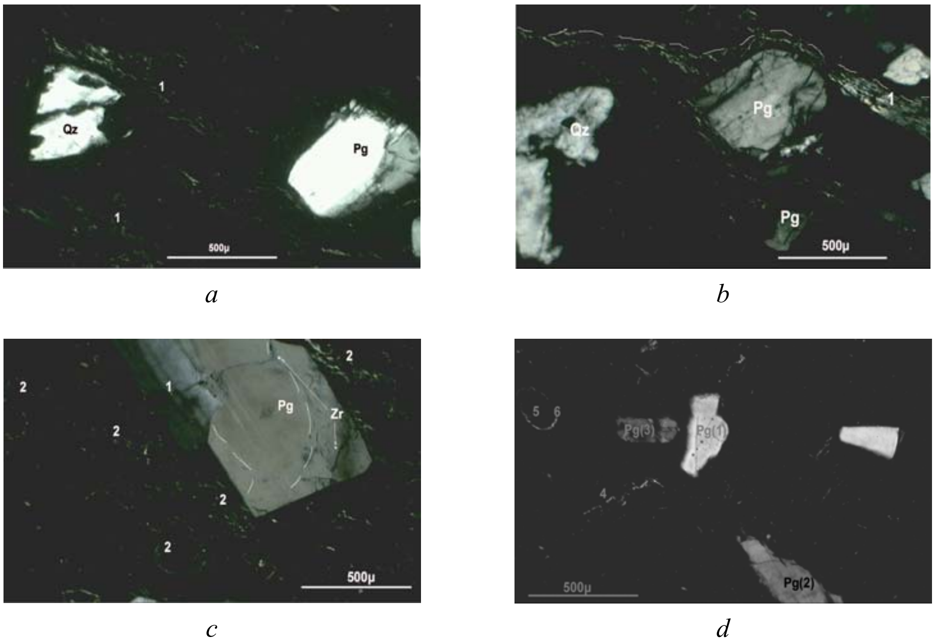


Fig. 4 – Thin sections of zeolitic tuffs: *a* – Plagioclase Feldspar (Pg) (twins and zone), quartz (Qz) and alteration product(1) (zeolites possible)(N+); *b* – Fissurated Plagioclase (Pg) quartz (Qz)and alteration product along fissures (1) (possible zeolites forming by the alteration of the glass) (N+); *c* – Plagioclase (Pg) zeolitization afected (yellowish colour) ; Zircon); fissures in plagioclase (1); alteration minerals (2- zeolites possible) (N+); *d* – fissurated and twins Plagioclase (2 and 3), zeolitizated (1), alteration product (4) (zeolites possible); volcanic glass vezicle (on the external side) and zeolites (inside) (N+).

In general, rocks with zeolites have a matrix of fine zeolite crystals which cement the rest on non- nezeolitic particles and influence the mechanical properties of the material (Colella *et al*., 2001).

2.4. The Water Absorption of the Tuffs

The size of zeolite pores and the amount of water they contain represent factors that directly affect water absorption and ion exchanges. They can remove crystalisation water and take it back without having essential changes in their structure.

Măicăneanu *et al*., (2008), consider the loss of water from the zeolites (with no alteration in the crystalline structure) at the temperature from 100ºC to 600ºC. At higher temperatures, the loss of water leads to deformations or alterations of the structures and the formation of neominerals.

The water absorption capacity was determined on zeolitic tuff (from Macicas quarry) aggregates obtained by sieving and sorting (at sizes of: 2...4 mm; 4...8 mm; 8...16 mm; 16...32 mm), according to SR EN 1097-6 (Fig. 2).

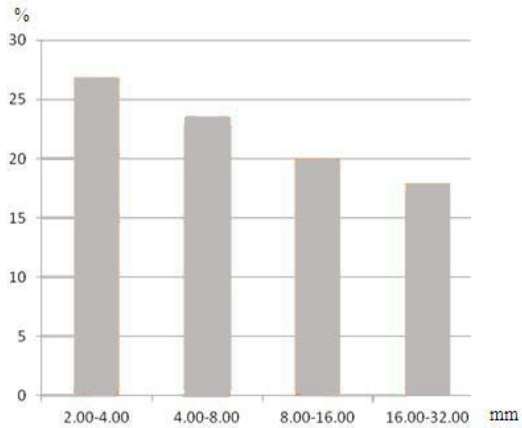


Fig. 5 – The water absorption of the tuffs.

Water absorption increases during the time, depending on the grain size and immersion time, the highest levels of specific absorption being found in small size zeolitic tuff particles. This aspect can be explained by the small particles whose specific surface is larger than that of samples of higher grain sizes; pores are shorter and more quickly saturated.

Volcanic tuffs represent thermally efficient materials, having a low conductivity, due to high porosity, resulted from high zeolite content (over 70% zeolites in analysed sample) *versus* other building materials (ceramic bricks, steel, concrete) and making the interior environment more comfortable.

The tuff high thermal stability is not owed to the nature of the exchanging cation, but rather to the stiff three dimensional lattice of continuous zeolites are (Măicăneanu *et al*., 2008).

The capacity of building members built with zeolites to damp the oscillation amplitude of the external temperature to be felt inside at low values and delayed in time as well as the capacity of envelope and partitioning elements to collect, store and release the heat are mainly due to the thermal properties of zeolitic tuffs. They have the property of absorbing heat (probably due to the height porosity and presence of zeolitic water, contents) during daylight and giving it out during the night, leading to heat stability in the summer season.

2.5. Compressive Strength of Zeolitic Tuffs

To define the mechanical properties of the tuffs, tests were performed for compression having the size 50 × 50 × 50 mm; the results range between 15.58 and 18.38 N/mm^2 (STAS 6200/3-81).

Though the mechanical properties of zeolitic volcanic tuffs are comparable to those of other materials (bricks, some concrete class), they are still not used at the same scale.

Low thermal conductivity (λ = 0.47...0.65 W/mK) and low embodied energy (embodied enegy coefficient = 0.6 MJ/kg), make zeolitic volcanic tuffs a material suitable for low energy consumption buildings needed to heating and/or cooling them, and it is the zeolites that contribute massively to the thermal stability of the rooms in question.

These tuffs can also be used to prepare masonry mortars and light concrete (as aggregates or cement substitutes, to prepare trass, foam cell concrete (due to its low heat conductivity) of sound or acoustic insulation materials or for ornamental purposes.

One of the detrimental aspects in the use of volcanic tuffs lies in its high water absorption capacity and low resistance to repeated freezing – thawing cycles.

2.6. Final Conclusions

Due to their mechanical and thermal properties, zeolitic volcanic tuffs are implemented widely, in the entire world, in areas near to crop outs, so that their local use is made easier.

The wide spreadout in the territory of Romania, the large local resources, the exploitation conditions in quarries, the low cost of excavation, the simple technologies (of grinding, cutting, etc.) and diminished incorporated energy as compared to other materials, make tuff be regarded as advantageous in the field of building materials (for concrete or cement production), or as a natural building stone to be used in ecological buildings construction.

REFERENCES

Anastasiu N., *Minerale şi roci sedimentare – Determinator*. Ed. Tehnică, Bucureşti, 1977.

Bărbat A., Bengeanu M., Marton A., *Modern Trends in Turning to Best Account the Volcanic Tuffs of Transylvania. Results obtained in : The Volcanic Tuffs from Transylvanian Basin, Romania*. The Geological Formations of Transilvania, Romania, 3, Cluj-Napoca, 1991, 383-390.

Bedelean H., Măicăneanu A., Stanca M., Burca S., *Tufurile vulcanice zeolitice, din judeţul Cluj, materii prime naturale, depoluante*. Grant CNCSIS, Res. Rep., 2005.

Colella C., de Gennaro M., Aiello R., *Use of Zeolitic Rocks in the Building Industry*. In: Bish D.L., Ming D.W. (Eds.), *Natural Zeolites: Occurence, Properties, Application*, Rev. in Mineral. a. Geochem., **45**, 551-587 (2001)

De Gennaro R., Cappelletti P., Cerri C., de Gennarro M., Dondi M., Langella A., *Neapolitan Yellow Tuff as Raw Material for Lightweight Aggregates in Lightweight Structural Concrete Production*. Appl. Clay Sci., **28**, Elsevier, 309-319 (2005).

Măicăneanu A., Bedelean H., Stanca M., *Zeoliţii naturali. Caracterizare şi aplicaţii în protecţia mediului*. Ed. Presa Univ. Clujeană, Cluj-Napoca, 2008.

Mârza I., Meszaros N., *Les tuffs volcaniques de Transylvanie, historique, valeur théorique et practique dans le développement de la géologie transylvaine*. The Volcanic Tuffs from Transylvanian Basin, Romania, *3*, Cluj-Napoca, 1991, 11-22.

Mohanu I., Georgescu M., Mohanu D., Manolache L., Drăgănoaia C., *Caracteristici fizico-mecanice şi estetice ale unor mortare pe bază de var-calcar-tuf vulcanic*. Rev. Română de Mater., **41**, *4*, 332-345 (2011).

Mumpton F., *La roca magica: Uses of Natural Zeolites in Agriculture and Industry*. Proc. Natl. Acad. Sci. USA, **96**, 3463-3470 (1999), Coll. Paper (http://www.pnas.org/content/96/7/3463.full.pdf).

Răcătăianu C.P., Benea M., Koch R., Peter A., Brandlein P., *Romanian Natural Building Stones*. *Geology, Rock types, Quarries, Companies and Products*. Vol. **I**, Transylvanian Region , Erlangen, 2007.

* * * *Încercări pentru determinarea caracteristicilor mecanice şi fizice ale agregatelor.* Partea **6**: *Determinarea masei reale şi a coeficientului de absorbţie a apei*. SR EN 1097-6: 2002.

* * * *Piatra naturală pentru construcţii – Luarea probelor, confecţionarea secţiunilor subţiri şi a epruvetelor*. STAS 6200/3-81.

CARACTERISTICI ALE TUFURILOR VULCANICE ZEOLITICE UTILIZATE ÎN CONSTRUCŢII

(Rezumat)

Necesitatea tot mai crescuta de înlocuire a unor materiale existente pe piaţă (cărămizi ceramice, oţel, beton) cu materiale care au energie înglobată redusă şi capacităţi bune de izolare termică, a impus valorificarea resurselor locale. Astfel, se abordează studiul tufurilor vulcanice zeolitice din cariera Macicaş (NV de Cluj-Napoca) din perspectiva valorificării lor ca materiale de construcţie naturale şi totodată ecologice. Probele au fost analizate sub aspectul caracteriticilor fizice şi mecanice. S-au realizat: difracţii de raze X (RDX) care au evidenţiat compoziţia mineralogică a tufului analizat şi mai ales conţinutul ridicat de zeoliţi (clinoptilolit – 63.72% şi phillipsit – 11.05%), analize microscopice pe secţiuni subţiri care au permis observarea proceselor de alterare a sticlei vulcanice, a feldspaţilor, micelor şi cuarţului (zeolitizari), SEM-uri care au evidenţiat tipul de zeoliţi care cristalizează în golurile tufului (Clinoptilolit). Determinările efectuate (densitate, porozitate, absorbţie de apă, conductivitate termică, rezistenţă la compresiune) şi mai ales conţinutul ridicat de zeoliţi (peste 70%), au evidenţiat calităţile acestor tufuri ca fiind comparabile cu ale altor materiale de construcţie.