

## THE IMMATURE CRYSTALLIZED SUBSTANCES INFLUENCE CONCERNING THE FEATURES AND PROPERTIES OF THE VOLCANIC ZEOLITIC TUFFS

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This paperwork proves the presence alongside of the clinoptilolite, of amount fine crystallized silica in the Piatra Verde – Slănic zeolitic tuffs. This quantity of the fine crystallized silica causes the appearance a „Hump effect” on the X-ray diffraction patterns in the range of the 15–35° (2θ angles) and confers to this zeolitic tuff a good pozzolanic activity. Pozzolanic activity together with the good ionic exchange capacity could represent the premises of complex utilizations. Generalizing, there is expectation that all volcanic zeolitic tuffs with this type of the XRD patterns, such as volcanic tuffs from Piatra Verde – Slănic ( the “hump” in 15–35° 2θ domain ), to be chemically active and to have a good pozzolanic activity.

*Key words:* Clinoptilolite; Fine crystallized silica; Pozzolanic activity.

### INTRODUCTION

The purpose of this work is to demonstrate the presence of a microcrystalline insufficiently crystallized silica in the Slănic tuff, only suggested in the previous scientific works; its existence explains the good pozzolanic activity of this tuff.

One of the natural resources of our country which could be used in a lot of practical utilization is the volcanic tuff. The main component is represented by the amorphous volcanic glass, to which the crystalline part joins. In this crystalline part there prevail: feldspars, quartz, muscovite, biotite, calcite and limonite. Among the zeolites, in more quantity is clinoptilolite<sup>1</sup>.

Clinoptilolite is the most known natural zeolite, it is found especially in some volcanic rocks in the concentration of the 60–90%. In Romania there

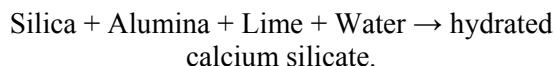
important occurrences of the volcanic tuffs with a 70% average clinoptilolite content<sup>2</sup>.

The volcanic tuffs also known as “cinerite” are considered volcano-sedimentary rocks, because of their mineralogical origin and sedimentary due to the way they were formed. The ash resulted from the volcanic explosive activities was transported by the wind and was deposited in various sedimentary environments such as subaerial, lacustrine, maritime<sup>3</sup>.

Despite that the natural zeolites can be found in other kind of rocks such as magmatic or metamorphic, the volcanic tuffs remain the most valuable deposits for these minerals. Because of this, it is not to be wondered why in the developing process of research the name of sedimentary host rock has disappeared; the most used name is that of “zeolites”, “natural zeolites” while “zeolitic tuffs” or “devitrified tuffs” are less used<sup>3</sup>.

The volcanic tuffs mixed up with water and lime has capacity to harden developing a strong silicates texture. There is a good parallelism between SiO<sub>2</sub> content able to react and the pozzolanic activity of volcanic tuffs.

The pozzolanic reaction of the volcanic tuffs could also be schematically represented like this:



Among pozzolanic reaction products of the pozzolanic reaction there can be enumerated: hydrated calcium silicate, hydrated tetrasilicic aluminate and infrequent, gehlenite, ettringite, etc.

The pozzolanic reaction is conditioned by thermodynamics factors, such as the energy difference between the initial and final state/phase, the grading distribution and kinetic factors. The bigger the energy difference, the faster the transformation into the hardened binder. The increase of the environment temperature has a positive effect on the kinetic of the hydration and consequently on the hardening of the binder<sup>3</sup>.

Activated cementations material – puzzolana binding systems, free of Portland cement, are at present a strong concern for ecological and energy-saving reasons<sup>4</sup>.

The equilibrium state of the solid state is the crystallized state. The amorphous state is not an equilibrium state, it appears as a result of kinetic factors, from the structural point of view being equivalent with liquid state. But, this (amorphous state) is recooled liquid, with a very high viscosity, so that the span of time for relaxing-disposition in the equilibrium crystalline structure is huge, often infinite, due to thermal diffusion displacement of the atoms.

Sometimes, transition processes could be observed, for example devitrifying phenomenon, i.e. crystallization of some glass<sup>5</sup>.

From the genetic point of view, volcanic tuffs components are classified in: primary components (pyrogenic compounds made of lava) and secondary components, formed by post-volcanic processes, which changed the primary cineritic material.

*Primary compounds.* These components are classified in two categories: amorphous and crystallized. The amorphous components are represented by volcanic glass. Practically this content represents the quantity of volcanic glass which remained unchanged during the post-volcanic processes. So, unaltered glass content is the proof of the intensity of these processes.

*Crystallized components* (crystalloclastic rocks). From the mineralogical point of view, these (crystallized components) in the case of the Slănic tuffs, are represented by: quartz, feldspars, biotite and muscovite.

*Secondary components.* The constitution of these components is the result of the volcanic glass transformation during of the post-volcanic processes. This transformation take places under two main conditions: devitrification (crystallization of the amorphous component, determining the appearance of the fine crystallized SiO<sub>2</sub> variety) and zeolitisation (transforming volcanic glass into zeolites, mainly clinoptilolite).

However, the content of secondary minerals could be deduced from the interpretation of the XRD patterns and it is the expression of the transforming processes which affected the rock in post-volcanic stage.

The particularities of the Slănic tuff consist in the high zeolites content due to transforming processes of the initial volcanic glass<sup>6</sup>.

## MATERIALS AND METHODS

### Apparatus

– DRON-2 Diffractometer with interface having the following parameters: different anticathodes (utilized radiation CoK $\alpha$ ,  $\lambda= 1.78890\text{\AA}$  and CuK $\alpha$ ,  $\lambda= 1.54182\text{\AA}$ ), Ni radiation filter, time constant 2s, continuous recording, accuracy in 2 $\theta$  angle measurement 0.01 degree. The identification of phases in the samples was made by the use of the diffraction database ICDD-JCPDS.

– ESEM XL 30 TMP Scanning Electron Microscope, equipped with an EDAX attached spectrometer.

### Materials

- Tuff samples from the Slănic, Piatra Verde quarry;
- Tuff samples from the Apostolache aria;
- Prepared tuff samples (see the work procedure);
- Common fine powdered glass.

## DESCRIPTION OF THE WORK PROCEDURE (METHODS)

### The I<sup>st</sup> experimental section

The tuff samples, collected from the Slănic Piatra Verde quarry and Apopstolache aria, were examined, using Scanning Electron Microscopy (SEM) and X-Ray Diffraction analysis (XRD), methods used until now in various other works<sup>6-9</sup>, but this time with upgraded apparatus.

### The II<sup>nd</sup> experimental section

Using a Cu anticathode, a few XRD analysis were carried out to samples obtained by progressively addition of common fine powdered glass to raw Slănic tuff (see Table 1).

Table 1

Composition of the prepared tuff sample for XRD analyses

Sample no.	Prepared tuff sample	
	Slānic raw tuff content, %	Added glass, %
Al-1	100	0
Al-2	66	33
Al-3	50	50
Al-3	33	66

For these 4 prepared samples XRD analyses were performed, with the same apparatus and in the same working conditions (Figs. 5–8).

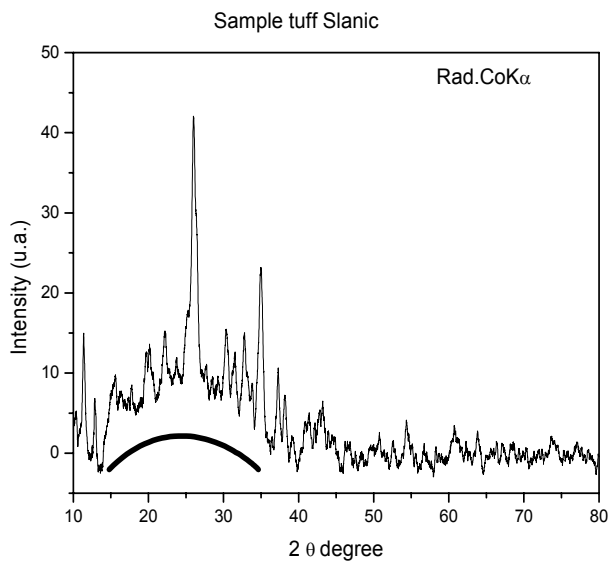


Fig. 1. Characteristic XRD pattern of the Slānic tuff.

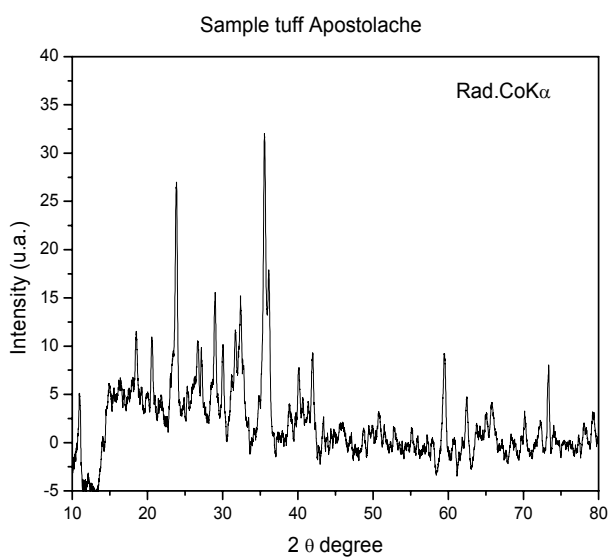


Fig. 2. XRD pattern of the Apostolache tuff.

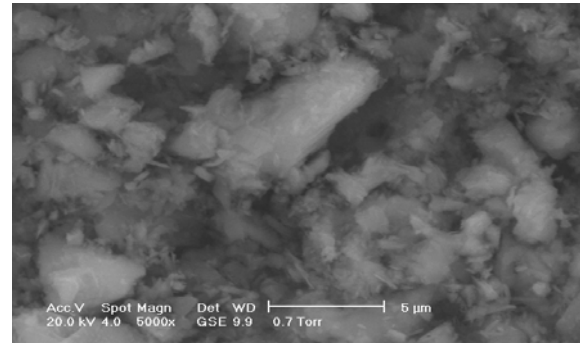


Fig. 3. Electron micrograph of the Slānic tuff (5000×).

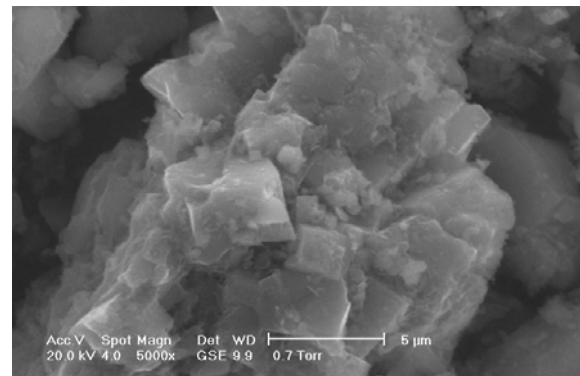


Fig. 4. Electron micrograph of the Apostolache tuff (5000×).

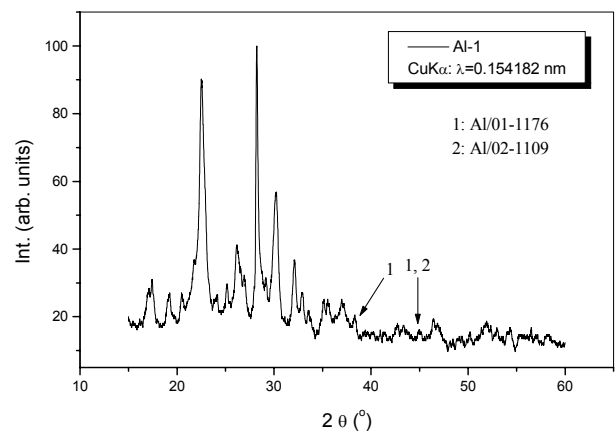


Fig. 5. XRD pattern of the prepared sample no. 1 (Al-1).

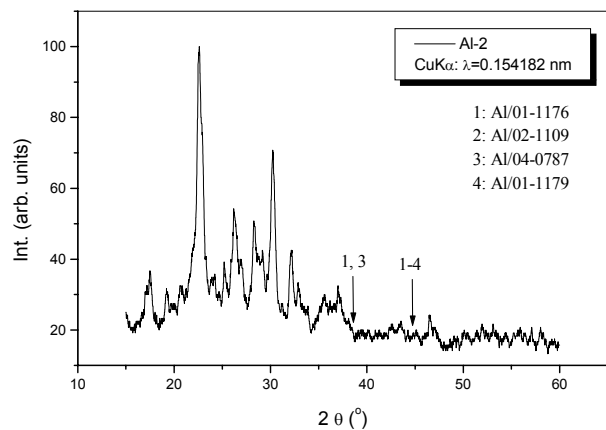


Fig. 6. XRD pattern of the prepared sample no. 2 (Al-2).

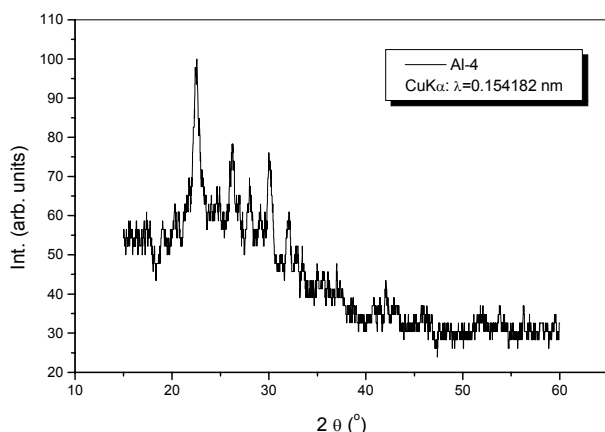


Fig. 7. XRD pattern of the prepared sample no. 3 (Al-3).

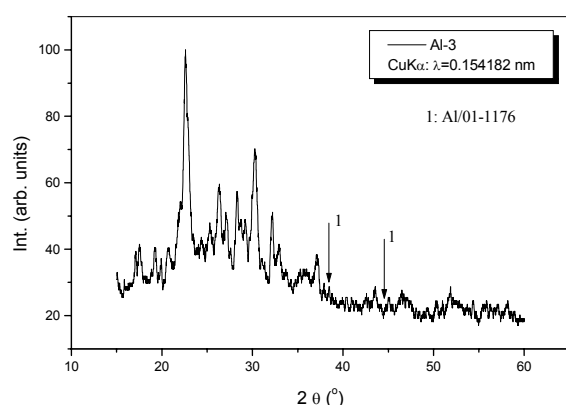


Fig. 8. XRD pattern of the prepared sample no. 4 (Al-4).

## EXPERIMENTAL RESULTS

### The I-st experimental section

Both SEM and XRD with different anticathodes (Co, Cu), applied to the Slănic – Piatra Verde tuff reconfirmed the presence of the clinoptilolite due to specific habit at SEM and due to diffraction peaks at XRD known from previous scientific works. A careful examination of the XRD patterns brings interesting novelties regarding to the composition of this zeolitic tuff, which distinguishes it from other zeolitic tuffs.

*Electron Microscopy.* Comparing obtained images by electronic microscope, it could be found that the crystallites size in case of the Slănic tuff ( $d < 5\mu\text{m}$ ) is smaller than Apostolache tuff crystallites ( $d > 5\mu\text{m}$ ), these particularities creating a more enhanced contact surface related to their volume (see Figs. 3 and 4).

*XRD analysis.* XRD analysis shows an especially interesting particularity of the Piatra Verde tuff – that is the “hump effect” expressed by accentuated rise of the Röntgen-amorphous background in  $2\theta$  angle range  $15\text{--}35^\circ$  (see pointed section with curve bold line from the Figure 1). For comparison it is presented XRD pattern of the zeolitic tuff from adjacent area (Apostolache tuff, see Figure 2), carried out in the same conditions and with the same apparatus<sup>10</sup>.

### The II-nd experimental section

The prepared sample no.1 has a slight, hardly visible rise of the Röntgen-amorphous background in  $2\theta$  angle range  $15\text{--}35^\circ$  section (Fig. 5).

The samples 2 and 3, show a perceptible background rise on the  $15\text{--}35^\circ$  degree section, in accordance with to the glass addition (more emphasized for the no. 3 sample) and the appearance of diffractions peaks superpositions is observed outside of the  $15\text{--}35^\circ$  degree domain (Figs. 6 and 7).

The sample no. 4 has an exaggerated rise (a real **hump**) and diffractions peaks superpositions are observed too, but on the entire domain  $10\text{--}60^\circ$  this time (see Fig. 8).

## DISCUSSIONS OF THE RESULTS

*The electron microscopy.* Regarding the chemical properties of the solids, it is known that there is not absolute inert solid, even when it is crystallized, for the atoms situated in the peripheral blanket of the solid do not have bound energy three-dimensionally satisfied like the atoms inside the crystals; thus the bound energy remains free and consequently active from the chemical point of view. This activity manifests itself all the more that ratio between total surface of the crystallites and volume is higher. In this way, mineralogical crystallized components very finely divided and therefore with very high surface in respect to their volume (such as crystallites from the Slănic tuff) are active because of their fineness.

*The XRD patterns.* The phenomenon of marked rise of Röntgen-amorphous background only on the  $15\text{--}35^\circ$  degree section and not on the entire domain of  $2\theta$  angles, (a phenomenon that was called here “hump effect” by the authors) proves the existence of immature crystallized nuclei and not the existence of amorphous silica in the true sense of the word.

As seen before in electron microscopy images, the crystallites have smaller dimensions than those of other tuffs. Only better crystallized silica performs peaks at the XRD analyses (with  $I/I_0 = 100$  at  $d = 4.05\text{\AA}$  for cristobalite and respectively  $d = 3.34\text{\AA}$  for  $\alpha$ -quartz)<sup>11,12</sup>, other having smaller in dimensions perform only this mentioned Röntgen-amorphous background rise.

The progressive, deliberate addition of the amorphous silicates (fine powdered glass), proves that the light rise of background on the  $15\text{--}35^\circ$  degree domain of  $2\theta$  angles, called by authors **hump effect**, is due to an amorphous or insufficiently crystallized low-dimensions silica. But the SEM images presentation of the raw Slănic tuff sample (Fig. 3) and the good total ionic exchange capacity (about  $100\text{--}150\text{ meq}/100\text{ g}$ ) mentioned in various scientific works<sup>6-9</sup>, are the reasons which lead us to believe that in reality there is a low dimensions crystallites quantity and not amorphous silica in the true sense of the word.

## CONCLUSIONS

As far as quantity is concerned, from the XRD data the participation of clinoptilolite was estimated at 60–70%, which is in accordance with the estimations of 60–90% made by other researchers in previous works<sup>6–9</sup>. Barbat and Marton, very familiar with the Mîrșid tuff, consider the Slănic tuff to be similar to Mîrșid tuff, with maximum values for the clinoptilolite of 70–80% and an average of 60% of the deposits<sup>3</sup>.

This quantity of microcrystalline silica thoroughly explains hydraulic properties and very good pozzolanic reaction of the Piatra Verde – Slănic tuff, which together with the good ionic exchange capacity, confirmed by various other scientific works<sup>6–9</sup>, could represent the premises of some special applications concerning the complex utilization of the zeolitic volcanic tuff, such as the nuclear decontamination of some streams contaminated with radionuclide and their safe stocking.

Generalizing, there is expectation that all volcanic tuffs with this type of the XRD patterns, such as volcanic tuffs from Piatra Verde – Slănic (the “hump” in 15–35° of 2θ domain), to be chemically active and to have a good pozzolanic activity.

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## REFERENCES

1. Naum N., Bâlba N., Onu P., Ababi V., Luca C., “Testarea tufurilor vulcanice pentru stabilirea posibilităților de utilizare ca adsorbanți pentru purificarea solvenților”, Contract de cercetare nr. 23677/79, Institutul Politehnic „Gh. Asachi” Iași, **1979**, 4–5.
2. Cobzaru C., Oprea S., Hulea T., Hulea V., Dumitriu E., *Aplicații ale zeoliților naturali în eliminarea metalelor din apele uzate și în catalizarea unor reacții chimice organice. I. Reținerea ionilor metalici pe clinoptilolit natural*, Revista de Chimie, București, **2002**, 53/10, 674–677.
3. Bărbat A., Marton A., “Tufuri vulcanice zeolitice”, Editura Dacia, Cluj-Napoca, **1989**, 16–19, 52–53.
4. Stoleriu S., Teoreanu I., *Procese de întărire ale sistemelor cu lianți fără ciment Portland*, Revista de Chimie, București, **2006**, 57/6.
5. Vainstein B.K., “Cristalografia modernă” (traducere din limba rusă), Editura Științifică și Enciclopedică, București, **1989**, 31–32.
6. Constantinescu E., *Mineralogical and petrographic studies of the badenian tuffs from the Getic Subcarpathians in order to their using in economic circulation*, Analele Universității, București, **1995**, 33–36.
7. Bedelea I., Stoici S.D., “Zeoliții”, Editura Tehnică, București, **1984**, 28–29, 102–103.
8. Cosma R., Hâncu, L., *Zeolititele de la Piatra Verde – Slănic*, Mine, Petrol și Gaze, **1985**, 36/11, 540–543.
9. Matei L., “Depozite de reziduuri toxice și radioactive realizate din materiale minerale”, Contract 33379/2004, code CNCSIS 300, **2004**, 5–7.
10. Mocanu B., Georgescu O., *Presence of the chabazite in the volcanic zeolitic tuffs from the Apostolache area*, Petroleum-Gas University of Ploiești Bulletin, Technical Series, **2006**, 58/3, 107–111.
11. ASTM Table-card 11-695.
12. ASTM Table-card 5-0490.