

USING FTIR, FT-RAMAN AND XRF TECHNIQUES FOR CHARACTERIZATION OF A PERLITE BEARING CONSTRUCTION MATERIAL AND ITS SOURCES OF PROVENANCE

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Berislăvești Monastery is a valuable monument of late feudal architecture, founded by the boyar Sandu Bucșenescu and his wife Maria. The monastic complex is located 8 km from Călimănești, in Berislăvești commune, Vâlcea, Romania. Recent rehabilitation works of the cell complex highlighted the need for some restorations. For characterizing the materials and finding the most inspired restoration solutions, a series of samples were extracted. Some are new renovation plasters, applied to the lower part of the wall on the west side of the complex, on the face from the inner courtyard of the monastery, and others are original plasters (probably dating from the interventions carried out during the 20th century), from the eastern side of the enclosure wall, the outer face. Although the general appearance of the plasters was very similar, the petrographic analyzes showed that the plaster used for the western wall includes, besides lime mortar, an unknown material in its composition, unlike the eastern wall of the enclosure. It was most likely a constructive solution that would confer an improved behavior concerning a permanent contact with meteoric waters. FTIR, FT-Raman and XRF techniques, were able to highlight the entire composition of the plaster on the western wall. It includes perlite, a natural material that, through thermal treatments, leads to an expanded form, with heat-insulating and sound-insulating properties. Perlite is an amorphous volcanic glass that, through the thermal expansion process, loses water and acquires a light structure, with a density several times lower. It is a non-renewable material, the best-known sources of raw material in the context of the Romanian construction market being: China, Turkey, Greece, Hungary. Extraction quarries are also known in Romania, although the main sources are exhausted. The comparative analysis of FTIR, FT-Raman and XRF spectra on sintered materials from different origins were able to establish the composition, the specific impurities and finally the source of the original perlite used in the plaster formation. Most probably it originated from Romania. Chemical analyzes completed the information regarding the recipe: 25% white granules and fine sand / mineral bearing impurities, and 75% calcite in the final plaster. In principle, compared to the original recipe: 1/3 granules and 2/3 quicklime. The heating of the granules to remove water, assuming the existence of the amorphous form $\text{SiO}_2 \cdot n\text{H}_2\text{O}$, and the subsequent mixing in quicklime, was highlighted. Application and hardening can produce the removal of water not only by drying, but also by three-dimensional distribution in the mass of the plaster during restoration of amorphous silica.

For the mortar sample (Figure 1), the following preliminary analyzes were performed:

- Determination of the approximate density;
- Separation into distinct fractions having different physico-chemical properties;
- Estimation of weathered mortar composition.



Figure 1. The initial mortar sample

Approximate density = 0.47 g / cm^3

Fractions identified in the mortar:
majority fraction = carbonates obtained after the mortar hardening into construction;
minority fraction = natural, inorganic material, consisting of white, solid, unitary fragments, of low density and with rounded edges (Figure 2);
fraction in traces = fine sand.



Figure 2. Separated white granules after physico-chemical pre-treatments

The specific recognition reactions in the laboratory and XRF / ATR-FTIR spectrometry led to convergent conclusions regarding fractions chemical composition:
the majority fraction = calcite;
the minority fraction = amorphous volcanic glass, most likely expanding perlite;
trace fraction = fine sand, quartz.

Based on stoichiometric calculations, for the analyzed sample, the final weathered composition can be estimated as follows:
68% slacked lime, 17% white granules (most likely expanded perlite-like structures, as will be demonstrated through subsequent analyses), 5% remaining fine sands, added intentionally or unintentionally, and approx. 10% of non-recoverable fractions; the organic fractions and accidental contaminants, are insignificant and are included in the difference up to 10%.
Based on the specific recognition reactions, the intentional additions of compounds having protein origin (egg white, casein) or vegetable (starch-based products) were not been identified.

In the second part of the study, some working hypotheses identifying perlite and its origin are issued, being confirmed / refuted by:

XRF measurements on perlite-like fraction isolated from mortar;
ATR-FTIR / FT-Raman instrumental analysis on the fractions separated in the form of small white particles, with rounded edges (granules of perlite-like fraction), chemically altered, and on the white-reddish solid fraction remained after their chemical digestion with concentrated hydrofluoric acid at high temperatures;
ATR-FTIR instrumental analysis and color reactions on the entire mortar fraction, shredded and homogenized.

In order to verify the hypothesis of the existence of perlite in the mixture, several varieties of perlite used in construction (P1—P6), of different origin, were procured. They were subjected to the same analyzes as the mortar and the fractions separated, such as expanded perlite.

By extrapolation, the most likely initial recipe is: 25% white expanded granules and fine sand / mineral impurities, and 75% calcite in the final mortar composition.

In principle, compared to the original recipe, the mass fractions become:
1/3 granules and 2/3 quicklime, water being added accordingly (considering the mass ratio of 100: 56 between calcite and quicklime, calcium oxide). It is not excluded, by referring to other observations, the heating of the granules to remove water, assuming the existence of the amorphous form of silica: $\text{SiO}_2 \cdot n\text{H}_2\text{O}$, and the subsequent mixing in slacked lime.
Application and hardening can produce the removal of water not only by drying, but also by three-dimensional distribution in the mass of the mortar during restorations, at least partially, of the amorphous silica, a process that takes place competitively with the exothermic carbonation reaction of slacked lime.

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XRF Results and Discussion

Sample code	MgO	Al ₂ O ₃	SiO ₂	K ₂ O	CaO	Fe ₂ O ₃
P6	2.15	13.81	71.24	7.06	0.583	1.73
P5	2.40	14.78	77.40	7.50	0.688	1.82
P4	1.83	15.65	76.72	6.07	0.993	2.43
P3	1.48	16.98	79.00	7.32	0.620	1.94
P2	2.04	15.35	59.48	4.67	1.08	4.91
P1	1.68	17.55	63.60	5.38	1.23	5.64
Average	1.93	15.68	71.24	6.33	0.865	3.08
Perlite mortar	2.57	1.50	18.06	0.430	3.28	Near 0

According to correlation coefficient between the Average value for the varieties of perlite, and the fraction isolated from the mortar, of 96.24%, we most likely have perlite in the mortar that has undergone various physico-chemical degradations throughout weathering and throughout laboratory pre-treatments.

Confirmation of the structure comes from ATR-FTIR and FT-Raman analyses.

Sample code	Description
P6	commercial expanded perlite IZOPER 2T, Procema Ilfov, Romania
P5	commercial expanded perlite IZOPER 2, Procema Ilfov, Romania
P4	commercial expanded perlite 70 middle fraction, Procema Ilfov, Romania
P3	commercial expanded perlite 90 fine fraction, Procema Ilfov, Romania
P2	expanded perlite from Turkey
P1	expanded perlite from Oaş (Oraşul Nou), Romania
Perlite mortar	perlite-like fraction isolated from mortar sample, Berislăvești Monastery, Romania

Perlite composition according to literature data:

70–75% silicon dioxide: SiO_2

12–15% aluminium oxide: Al_2O_3

3–4% sodium oxide: Na_2O

3–5% potassium oxide: K_2O

0.5–2% iron oxide: Fe_2O_3

0.2–0.7% magnesium oxide: MgO

0.5–1.5% calcium oxide: CaO

3–5% loss on ignition (chemical / combined water)[3]

ATR-FTIR & FT-Raman for mortar and perlite-like fraction; Results and Discussion

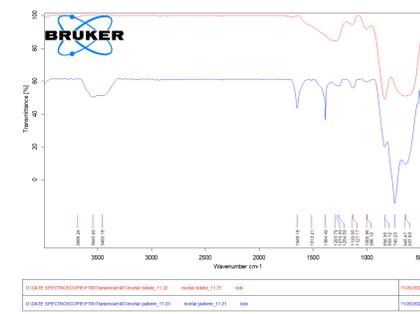


Figure 4. ATR-FTIR spectrum for the untreated powder mortar fraction (blue line) and the perlite-like fraction, chemically processed (red line)

The ATR-FTIR spectrum of the untreated mortar (Figure 4, blue line) presents complex signals in which some can be identified that are characteristic for calcium carbonate, iron oxides, expanded perlite, tectosilicates, quartz sand; in general, the classes of compounds whose oxides were highlighted by XRF.

In the spectrum of the processed perlite fraction (Figure 4, red line), some signals disappear, such as those of iron oxides, calcium carbonate, most tectosilicates (feldspars as degradation products), while the characteristic signals of expanded perlite are better highlighted, a fact confirmed by the corresponding spectra of samples P1-P3 (Figure 6) and literature data.



Figure 3. The reddish-white compound that remained after the purification of the white solid fragments from the mortar, similar to perlite

Using the Geomining operating mode, XRF spectrometry highlighted the characteristic oxides of perlite, whose total mass percentages lead to 99.14%, on average. The individual percentages fall within the ranges recommended by the literature. In the case of perlite-like structures, the summation leads to 25.87%, the individual percentages being affected by the physico-chemical treatments. In Figure 3, you can see the solid fraction that contains the degradation products of the expanded perlite.

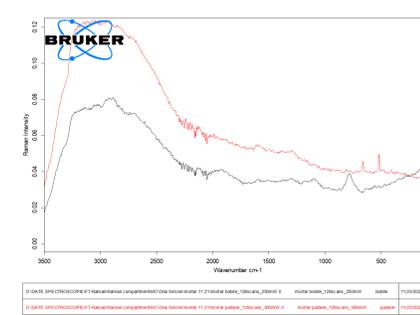


Figure 5. FT-Raman spectrum for the untreated powder mortar fraction (red line) and the perlite-like fraction, chemically processed (black line)

The FT-Raman spectrum of the untreated mortar (Figure 5, red line) clearly highlights the presence of calcium carbonate, the signals of the other components being diminished. Instead, in that of the perlite-like fraction, signals of thermally expanded and chemically treated perlite appear distinctly (Figure 5, black line). These signals should be interpreted in the context of the similar spectra for samples P1-P6 in Figure 7. The literature does not provide spectra for perlite, so it is worth the effort to be considered in the future.

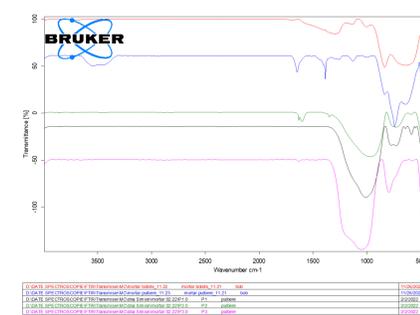


Figure 6. ATR-FTIR spectra for the perlite samples P1-P3; comparison with mortar and perlite-like fraction (different color lines)

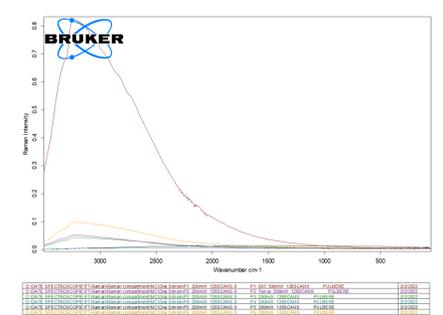


Figure 7. FT-Raman spectra for the perlite samples P1-P6 (different color lines)

A Bruker Vertex 70 FT-IR/FT-Raman spectrometer with solid rock interferometer was used. For FTIR, a KBr beam splitter and the method of pelletizing the sample in powder form (1 mg) with potassium bromide (300 mg) by pressing at 10t/cm² and the MIR probe were used for non-destructive testing in the spectral range 650 – 4500 cm⁻¹. The spectrometer is also equipped with the Raman module (RAM II) and Raman probe (RAMPROBE) for the non-destructive analysis of solid and liquid samples equipped with a NIR LASER excitation source with a wavelength of 1064 nm (Nd:YAG) and adjustable power between 1 and 500 mW, ultrapure German semiconductor detector cooled with liquid nitrogen.

A portable spectrometer with X-ray fluorescence and energy dispersive (EDXRF) TRACER Series model, TRACER 5i construction variant that uses a Rhodium-based X-ray generator, was used. The detector of the device is the Silicon Drift (SDD) type, positioned at an angle of approximately 45° to the normal reference plane and approximately 90° to the generator tube. A voltage of 40 keV was applied to the tube to obtain the incident X-ray beam. A collimator was used that restricted the diameter of the beam on the sample to an 8 mm diameter spot.

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