EVALUATION OF LIMESTONE WITH NON-INVASIVE ANALYTICAL METHODS

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The aim of this paper it was to determine the properties of the limestone in order to prevent deterioration during the time that may result from differentiated behaviors (mechanical strength, porosity, chemical and mineralogical composition), differentiated deformability (elasticity modulus), and chemical reactions with the environment (solubility and pressure crystallization) or with mortar used in the construction ("gypsum black crust"). In this study, fine limestone powder samples and rock samples were analyzed by classical methods (density, weight, volume, apparent density, porosity, water absorption, compressive strength, thin sections) and by non-invasive one (XRD, EDX, SEM) in order to characterize them in details.

Key words: limestone, X-ray diffraction, EDX analysis, SEM, thin setions.

1. INTRODUCTION

Due to the good appearance and proper physical and mechanical characteristics, limestone has been used since very old times as a building stone. However, as time goes on, they are exposed to damages, either by chemical dissolution or by physical or combined degradation. Atmospherically pollutants (carbon dioxide, nitrates and sulphates) emitted in the atmosphere after the burning of conventional fuels have increased values lately having damaging effects upon existing limestone building, accelerating their deterioration.

Durability of limestone can be affected during lifetime, being necessary to evaluate their mechanical, physical and mineralogical composition beginning with designing building stage in order to avoid their decay.

2. RESEARCH METHODOLOGY

Investigation techniques can be classified in two main categories: destructive and nondestructive methods.

2.1. DESTRUCTIVE TECHNIQUES

Destructive technique can be used in the investigation of mechanical characteristics (compressive strength), physical characteristics (water absorption, porosity) or mineralogical characteristics (thin sections) of limestone samples.

a) Physical-mechanical properties of limestone samples

Compressive strength of limestone, were performed according to STAS 6200/5-91 [1] on five cubic samples having the size 50x50x50 mm samples have been prepared in accordance to STAS 6200/3-81 [2]; the results range between interval 23.10 and 28.73 N/mm ^{2}.

Apparent density and apparent volume were determined using the hydrostatic balance on saturated, cubic shape specimens [according to STAS 6200/11-73] [3], while water absorption was determined according to STAS 6200/12-73 [4]. The values are presented in Table 1.

Table 1

Physical-mechanical properties of limestone samples

Limestone samples	Apparent density [g/cm^3]	Apparent volume [cm^3]	Water absorption [%]	Apparent porosity [%]	Compressive strength f_b [N/mm^2]
S1	2.24	17.25	3.52	7.88	27.56
S2	2.23	16.27	2.32	5.16	25.70
S3	2.24	19.32	2.11	3.90	28.73
S4	2.21	15.49	5.28	11.84	23.10
S5	2.22	15.95	2.23	4.25	24.34

b) Thin sections

Thin sections were made according to STAS 6200/3-81 [2] and studied with a polarizing microscope.

Limestone analysed in thin sections (Figure 1), is heterogeneous oolitic, bioclastic packstone type, with a predominantly carbonate binder as sparitic cement with mosaic forms to drusy, acicular.

Alochemic corpuscles are predominant: oolites (250 – 500 microns), pellets (50 microns), and extraclasts (biotic and oolitic intraclasts) with iron oxy-hydroxides pellicles. Frequently, the particles come into tangential contact and they have necrotic intergranular pores with sparitic calcite.

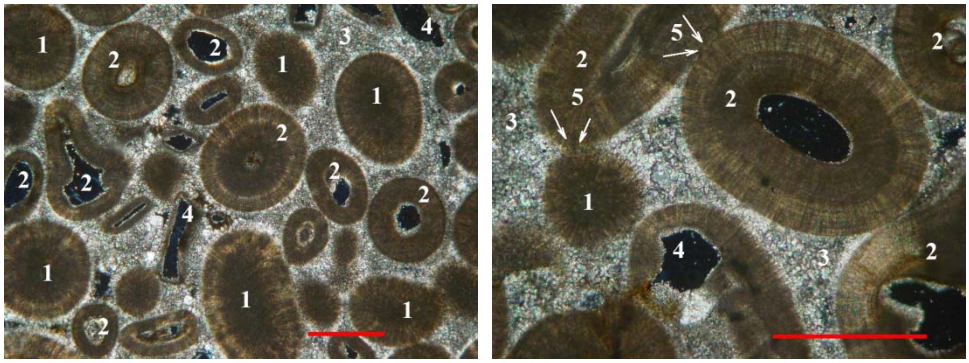


Fig. 1 – Thin sections of limestone sample (S2): 1 – oolites with core filled, 2 – oolites with empty core, 3 – sparitic carbonate binder, 4 – pores with calcite on the border, 5 – contact between oolites, scale bar 500μm.

Carbonatic detritic binder (less than 50 microns) contains oolites, bioclasts, rare grains of quartz and coarse carbonate.

It has mostly residual porosity, as the intergranular pores, of dehydration (fenestra structures) or of protection, are partially filled with calcitic drusy cement. A secondary porosity may form due to a diagenetic dolomitic metasomatosis. The poronecrosis occurred also due to pressure solubilization processes, parallel to the stratification, resulting in jagged boundaries between the oolites and dolomite micro granules deposits, which are more difficult to dissolve than calcite.

2.2. NON-INVASIVE METHODS

The non-invasive methods (XRD, SEM and EDX) are useful tools to determine the mineralogical or chemical compositions of different materials and have been used beginning with the ‘90 years in restoration of heritage buildings [5–6], medical domain [7], for space applications [8] or art and archeology [9].

The qualitative analyses in thin sections of building materials are incomplete due to polymorphic transformations of carbonate minerals, being necessary to complete them with X-ray diffraction (XRD), EDX and chemical composition analysis.

Non-invasive methods of analysis are preferable in such cases precisely because very small quantities of samples is required (several grams powder) with the possibility of rapid investigation.

These analysis techniques can be used to determine the mineralogical and chemical composition of rocks (qualitative and quantitative) and secondary mineralogical decays such as those produced by salts (efflorescence, gypsum “black crust”).

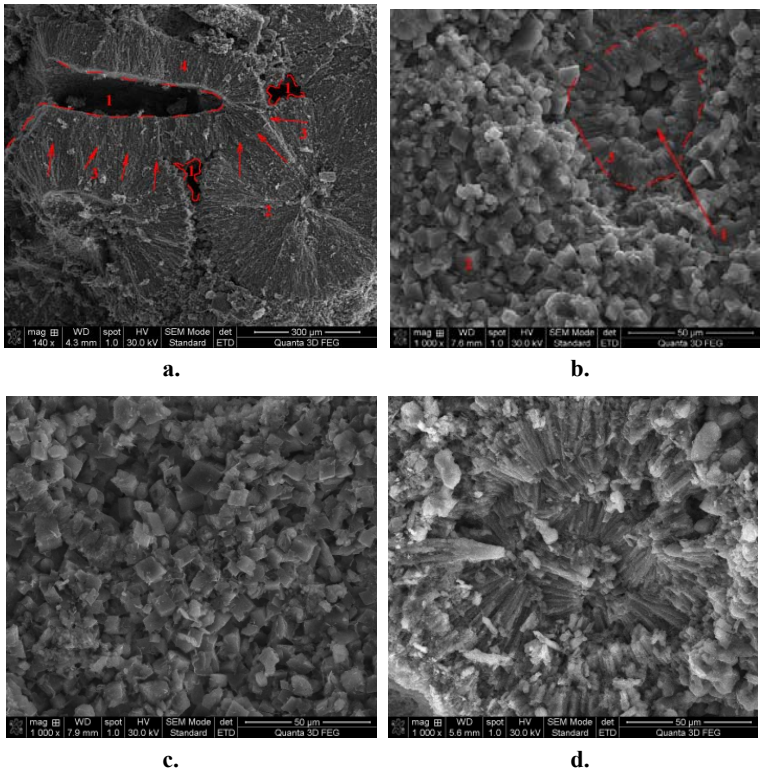
2.2.1. SEM – EDX analysis

Electron microscopy scan is a non-invasive method (SEM – EDX) which can be used to identify the three-dimensional structure of the new and old building materials.

The limestone samples were mounted on double-sided adhesive carbon discs, coated with a layer of 7 nm of Pt / Pd in an argon atmosphere by using an Agar Automatic Sputter Coater device. The samples were examined in an electronic microscope with Jeol JSM 5510LV scan, equipped with an elemental analysis system from Oxford Instruments Inca 300.

Oolites have a radial structure (Figure 2a,b), some with completely dissolved nucleus with prismatic crystals of calcite grown approximately normal to the boundary surfaces of the laminae. There is a concentration of the insoluble residue between the oolites which reduces the porosity of the limestone.

The crystallization of the pseudo hexagonal aragonite on the inner edges of the void formed in the oolites can only be observed in SEM analysis. In thin sections, the crystallization of a carbonate mass is visible, but without being able to specify the mineralogical species like calcite (Fig. 2b,c) or aragonite (Fig. 2b).

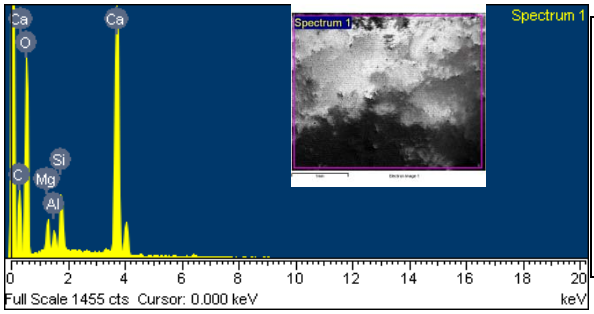


a. **b.**

c. **d.**

Fig. 2 – Images to scanning electron microscopy (SEM): a) 1- Pore, 2- oolites with filled core, 3- sutural contact between oolites, 4- oolites with empty core; b) 1- aragonite crystal, 2- calcite, 3- calcite on the pore walls; c) carbonate groundmass (calcite crystals); d) oolites having radial structure.

The chemical composition of the sample is expressed as oxides (Figure 3) and determined by attaching an X-ray detector (EDX, WDX) to the electronic microscope.



Element	Weight%	Atomic%
$CaCO_3$	13.64	21.18
SiO_2	53.10	61.91
MgO	1.89	1.45
Al_2O_3	1.00	0.69
SiO_2	3.20	2.12
Wollastonit	27.17	12.64

Fig. 3 – EDX analyses on limestone sample.

Analysis shows that the limestone sample has a low Mg^{2+} (lower than 4%) content, so it is a low magnesium calcite limestone.

The presence of iron in the form of iron hydroxides of iron in the fine limestone (micrite) determines the slightly reddish colour of the analysed limestone. This can be seen in the EDX spectra of limestone, but also in the thin sections in the form of iron oxy-hydroxides (fundamental mass and reddish brown oolites).

2.2.2. XRD analysis

In order to determine the mineralogical composition of mortars, a few grams of the sample were taken and semi-quantitatively analyzed by X-ray diffraction using a diffractometer with Cu-Ka radiation anticathode, λ = 1.548740 Å and $2^0\theta$/min from 10^0 to 70^0 (2theta).

In terms of mineralogical composition, XRD analysis of the limestone sample (Fig. 4) revealed the presence of calcite - 87.3%, quartz - 5.6%, feldspar - 7%, vermiculite –0.2%.

The X-ray diffraction did not reveal the presence of iron, either due to the colloidal state of iron oxy-hydroxides present in the limestone mass, or due to the small percentage (less than 4%) of cryptocrystalline new-minerals with iron that could not be recorded in the diffractograms.

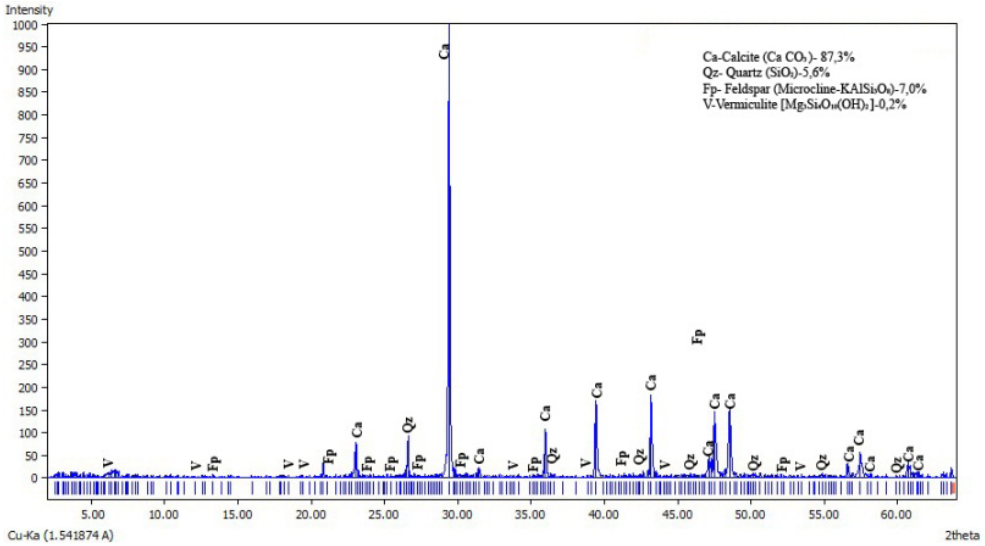


Fig. 4 – XRD analyses on limestone sample.

3. CONCLUSION

Detailed macroscopic investigation of construction materials by classical methods, often destructive, cannot provide sufficient data to assess their behaviour over time, requiring micro-structural analysis (SEM, EDX and XRD). On the other hand, non-invasive methods do not provide independently sufficient data necessary for assessing the structural elements.

The mineralogical thin section and SEM observations are compared and correlated with the X-ray diffraction analysis (XRD) and EDX spectra. These last techniques are used as complementary analysis for identification of the limestone crystalline phases and mineralogical content.

Interrelationships of the crystals can be observed only in scanning electron microscopy, in this way it can be determined the porosity of analyzed samples.

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