MICROSTRUCTURAL ANALYSIS FOR INVESTIGATION OF LIMESTONE DAMAGES – A CASE STUDY OF THE FORTRESS WALL OF CLUJ-NAPOCA, ROMANIA

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Received February 12, 2014

This paper presents the results of petrographic analyses performed on limestone samples originated from a heritage construction situated in Cluj-Napoca city. The purpose of the paper is to highlight the importance of using the microstructural analysis (thin sections, SEM analysis) as additional methods to the conventional ones (mechanical-physical determination), when the factors that lead to differing damaging of rocks are evaluated. The samples were investigated in thin sections, to the polarised light microscope, on fragments treated with Alizarin Red S as well as SEM analysis performed with the scanning electron microscope. The results found in investigated limestone samples highlighted the different percent of calcite and dolomite content and consequently the different degree of degradation of the rocks.

Key words: thin sections, SEM analysis, limestone, degradation, construction.

1. INTRODUCTION

Old constructions made from natural stone masonry have been exposed since the beginning until now to the physical, chemical and mechanical actions, which have affected their microstructural behaviour during the time.

Natural stones can present varying mineralogical features, even when they have the same quarry of origin. A simple microscopic analysis points out only to their structure, texture, density, porosity and colour, properties but do not provide sufficient information for the further microstructural level transformations. The details found in microscopic analyses are required to give additional data on the chemical, physical and biological reactions that can affect the natural stones.

In the last years Scanning Electron Microscopy (SEM) tests have been used on a large scale in fields like: medical science [1], metallurgy [2], archeology and construction [3–9]. This is an analytical tool, a non-invasive one, used in micro-analysis to study the materials decay, especially natural stone deterioration [3–9].

Rom. Journ. Phys., Vol. 59, Nos. 5–6, P. 608–613, Bucharest, 2014

In SEM test can be detect the pore structure, fine fracture of samples or to find information about mineral morphology and crystalline structures.

The paper shows the mineralogical analysis for several limestone samples originated from an existing heritage construction in the purpose of identifying the particular features of the stones as well as the factors leading to their degradation.

2. MATERIAL AND METHODS

For research, were collected some felt limestone fragments from the west part of the fortress wall, Baba Novac area. The fortress wall is an old monument built in XV–XVI centuries in three different epochs (1405–1449; 1470–1507; 1515–1525), with different material (different stones, mortars, bricks) specific to each period.

Large blocks of tuff, sandstone and mainly limestone as local material were used for wall construction to confer it the necessary stability and strength.

The masonry members have withstood weather conditions in time, but beginning with the industrial development of the city, the composition of the air was modified substantially, leading to acid rains and hence, an accelerated damage in the wall [10]. The most often transformations that occur are those related to gypsum crust formation or to the reaction of calcite with sulphites originating in the burning of the fossil fuel [10]. The moisture due to capillary rising (Fig. 1), the free-thaw phenomena are other causes that led to the degradation of limestone blocks.

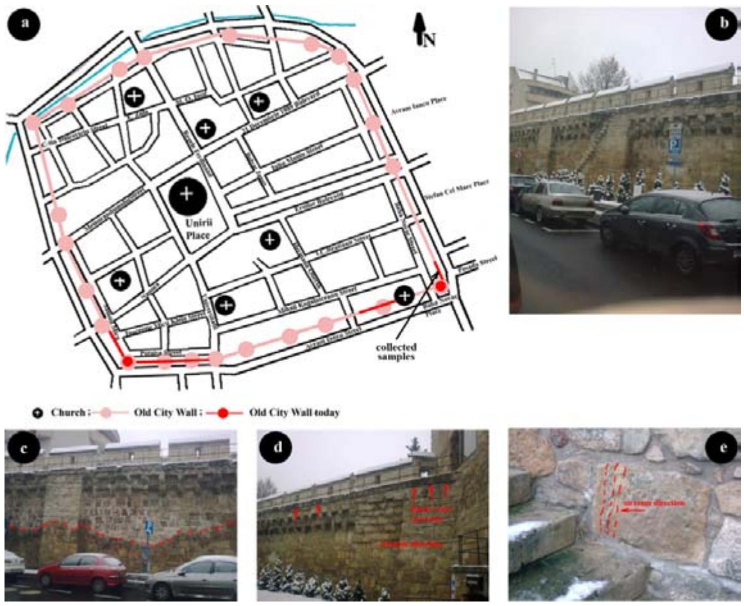

Fig. 1 – The fortress wall of Cluj Napoca, Baba Novac area, the west part of the wall: The initial wall plan (a), the west part of the wall (b), humidity due to capillarity (c), black crust (d), stratum direction perpendicular on the block orientation in the building (e).

From the limestone fragment collected, it were prepared thin sections, according to STAS 6200/3-81 [11] and analysed after that using a polarised light microscope, while the polished fragments were treated on the surface with Alizarin Red S solution to highlight the calcite/dolomite content.

SEM tests were performed using Agar Automatic Sputter Coater device. The limestone samples were placed on double face adhesive disks, covered by 7 mm Pt/Pd layers in argon atmosphere, then investigated with a Jeol JSM 5510LV scanning electron microscope.

3. RESULTS AND DISCUSSION

The thin sections, Alizarin Red S fragments and SEM analyses of limestone samples show the following results:

a) Sample A represents a grainstone type, containing: clasts of feldspar, quartz (200 microns), muscovite, carbonates, bioclast and micritic carbonate cement. Pores and voids tend to get filled with sparite, and hence remanent porosity occurs. Coarser quartz clasts contrasted to the micritic binder can bring about the detachment of the clasts and the occurrence of a larger secondary porosity (Fig. 2a, c). On the other hand, while watery, salty or acid solutions penetrate the pores, damage occurs because of the crystallisation pressure and of the chemical reactions with the calcite, respectively (the black crust). The limestone fragment treated with Alizarin Red S shows a high percentage of calcite compared to dolomite, and this suggests a higher sensitivity to the chemical attack of the external agents, *i.e.* acids (Fig. 2b).

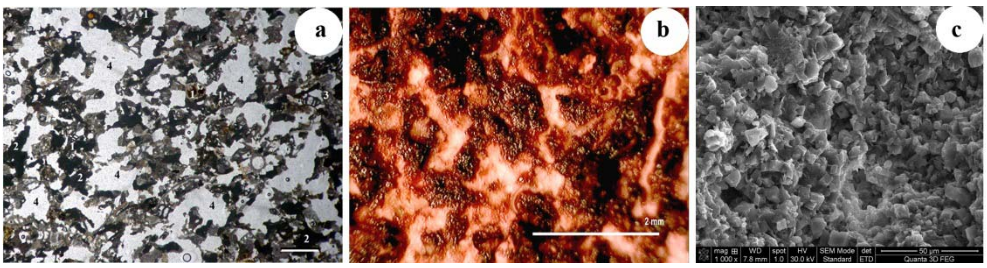

Fig. 2 – Sample A: a) Thin section: 1- bioclasts of benthic foraminifers, 2- fragments of red algae, 3- bioclasts of bryozoa, 4- secondary porosity, dissolution of the matrix, pore/ voids (The scale bare is 0,5mm); b) Alizarin Red S stained section: calcite red-orange /black coloured and dolomite uncoloured; c) SEM: voids and calcite crystals.

b) Sample B is a packstone with sparitic carbonate cement of drusic or mosaic aspect which contains: coated grains (50% of rock volume); ooides (500 microns) with detrital quartz or bioclastic cores, pellets, lumps (1 mm) and foraminifers bioclast mainly of 100 microns. The ooides, lumps and pellets of microcrystallin carbonate textures were coated by 10–20 microns wide sparitic mosaic or needle-like carbonate.

The porosity has a complex evolution. The primary intergranular and protection pores were totally or partally infilled by mosaic or drusic carbonate cement then by iron hydroxids. The remanent pores are of 500 microns length and 50 microns width, sometimes they are smaller about 100 microns (see Fig. 3a,c). Poronecrosis is outlined by pressure solution processes on ooides, on the stylolitic surfaces being infiltration of iron hidroxids (Fig. 3a).

Alizarin Red S section (Fig. 3b) shows a high number of ooides well outlined, and the percent of calcite (red-black colour) is higher than dolomite content (uncolored).

Fig. 3 – Sample B: a) Thin section of sample: 1- ooides, 2- bioclasts, 3- ooides wiht empty vortex, 3- sparitic mosaic calcite. The scale bare is 1mm; b) Alizarin Red S stained section: 1- sutural contact between ooides, 2- ooides (high number of empty or full ooide's cores); c) SEM: the core of one full ooide.

c) Sample C is a grainstone type heterogenous limestone, locally mudstone type (Figure 4). It contains: bioclasts (foraminifers of 50- 100 microns sizes), having sparitic carbonate infilling, carbonate intraclasts, ooides (200- 500 microns), lumps (1mm), broken, iron hidroxides - coated bioclasts of foraminifers. The mass ratio between the ooides and bioclasts it seems to be 1:1. The fine grained (mud) supported carbonate matrix contains quartz clasts (20- 30 microns), mica flakes and ooides of 20–50microns sizes.

The rock has a remanent porosity (20–50 microns sizes) with complex poronecrosis evolution. The primary intergranular pores of 1mm, were totally or partially filled by sparitic mosaic carbonate. Can also be observe a diagenetical dolomitisation imprinting (Fig. 4a,c), which can determine a secondary porosity, the later being filled by sparitic calcite. Along the ooides boundaries there are also effects of loading pressure, the pressure solutions observed in two ortogonal directions, marked by iron - hydroxids films. The main pressure solution effects are parallel with rock stratification (Fig. 1e), these effects also outlined by preferrential solubilisation of calcite-rich laminae in comparison with dolomitic laminae. It can be locally remark 10–20 microns wide veines of mosaic calcite resulted in poronecrosis of tension fissures.

The section with Alizarin Red S is almost equal coloured red-orange and uncoloured, that means the percent of calcite (red-orange) is almost equal to that of dolomite (uncoloured) (Figure 4b).

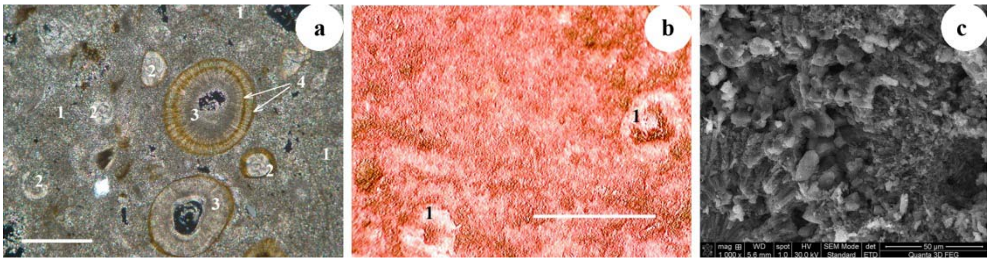

Fig. 4 – Sample C: a) Thin section: 1- sparite calcite, 2- bioclasts, 3-ooides, 4-iron hydroxides. The scale bare is 1mm. b) Alizarin Red S stained section: 1-poor content of ooides. The content of calcite is similar to that of the dolomite (percent of red/uncoloured zones are close). c) SEM: voids (right-down corner) and full core ooides (to the left corner).

4. CONCLUSION

The tests performed on thin sections, the SEM tests and the analyses of the fragments treated with Alizarin Red S lead to the conclusion that sample A exhibits a higher porosity and a higher calcite content compared to samples B and C. Sample B has a lower porosity then sample C, and the dolomitisation processes are more lighten. This also shows a higher degree of damage of sample A then samples B and C, due to calcite increased susceptibility of inter-reaction with the acids in the environment, as compared to the dolomite context.

The chemical reactions occurring in limestone are directly influenced by the moisture due to capillary rising or to rainwater stagnation at the surface of the rock.

Microstructural tests are essential in the stage of materials selection when new buildings are to be erected or older buildings to be retrofitted. This kind of tests can be complementary to the traditional methods as they provide supplementary information regarding the compatibility between the natural stones and their behaviour to the environment actions.

The porosity into thin section is completed with SEM analyses, by determining the pore volume, their distribution and size properties having influence in damage process of the material. Distinct from concrete members, where the direction of the pores does not much influence their behaviour under the action of rain water or underground water, in rocks and mainly in limestones (very soluble in contact with acid water), the direction of the pores (perpendicular to stone stratification) and especially the position of the stone in the construction, can affect significantly the behaviour of the construction damaging in different way the limestones used.

If the rock porosity is perpendicular to the stone stratification, then a limestone block placed horizontally will exhibit porosity along the direction in which rainwater falls. Thus, underground water or rain water can migrate into the capillary pores and fastening the decay of the stone.

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