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The Influence of Porosity and Bioclastic Contents on Limestones Decay

The limestone damages are a consequence of environmental factors and of the stone properties. The paper presents the analysis of few limestone samples from physical (density, water absorption, porosity and compactness) and petrographical (thin sections) point of view in order to determine the importance of porosity and bioclastic contents in stone behavior during lifetime. The analyzed samples had different rate of decay and was taken from existing constructions located in Cluj Napoca.

Keywords: decay, limestone, water absorption, bioclastic, porosity

1. Introduction

A stronger increase of toxic gases emissions (CO_2, SO_2, NO_x) in the atmosphere in the last years lead to the development of the acid rain and an accelerated damaging of existing limestone buildings. Statistical data shows a very increased value of the amount of total greenhouse gases in the interval 2000-2008 [10]:

- SO₂ from 134,17 tonne/year to 433,78;
- NO_x emission from 176,2 to 2422,6 and
- NH₃ from 0,001 to 3736,56.

Atmospheric pollutants combined with water from the atmosphere will produce acid rain, the main cause of limestone decay during their lifetime. Chemical dissolution, physical degradation (thawing-freezing, thermal shocks) or biological damaging (bacteria, lichens) are the most common types of limestone degradations observed in the existing constructions.

The moisture content of limestones and moisture distribution inside them are mainly influenced by their physical properties (hygroscopicity, porosity). Pore structure, pore size distribution and the limestone structures (clastic, granular and bioclastic content) controls the quantity of water absorbed and rock durability.

In Cluj Napoca area the most used limestone in constructions is of bioclastic type (which contains different bioclasts: foraminifera, ooids, red algae, bryozoa, echinoid and lithoclasts).

1.1 Physical decay

Physical decay of limestone is the consequence of complex and mixed actions: chemical actions, weathering (rain, relative humidity, capillary rise, technological water, accidental causes, and infiltrations), wind actions, sun light radiation and temperature fluctuations (thawing-freezing).

In the capillary pores (pores with radius of 10⁻⁷m to 10⁻⁴m), the circulation of the water is slow and during thawing, can develop pressures over 2000daN/cm² [1]. The thawing-freezing process leads to the degradation of surfaces soaked in water as the volume increases while passing from the liquid to the solid state for many times [3].

The wind action engages small solid particles, when the cementing materials holding the grains of sand together it breaks down, making the limestone more susceptible to fracturing (Figure 1).





Figure 1. Physical decay of limestone used in different building elements

Sudden temperature variations have a direct consequence upon the effect of dilatation-shrinkage resulting in this way some micro-fractures on the limestone surface, which can cause an increase of permeability and penetration of water inside the stone.

1.2 Chemical decay

Carbon dioxide passes into carbonic acid under the action of water, and, directly or indirectly, penetrates the stone through capillary action as polluted water. This effect can be accompanied by certain physical processes resulted as a reaction between the polluted water and limestone mineralogical compounds (Figure 2)[9].





The diluted carbonic acid dissolves the limestone, though limestone solubility in water solutions is tightly connected to their physical and chemical properties. Fred T. Mackenzie (2003) show that the aragonite (CaCO₃ -orthorhombic) is about 1.5 times more soluble than calcite (CaCO₃ -trigonal), while vaterite (CaCO₃ hexagonal crystal system) is about 3.7 times more soluble than calcite and 2.5 times more soluble than aragonite [7].

Even unpolluted rains contain carbon dioxide, which produces a weak carbonic acid (able to dissolve calcite) that, if combined with other atmospheric pollutants (sulphur and nitrogen oxides) can cause important damages of stone blocks and structural members.

Sulphates and derived salts are very dangerous for wet limestone component materials, especially when reacting with calcium carbonate ($CaCO_3$). The result of this reaction is the soluble calcium sulphate, the mechanism of rock destruction being indirectly influenced by the formation of the sulphur acid [4].

The calcium sulphate appears at the surface of the building elements as a black gypsum crust (Figure 3) [9].



Figure 3. The reactions of calcium carbonate with sulfuric acid

Normally, the gypsum recrystallisation pressure has the value 282 daN/cm², but, when formed by anhydrite rehydration, pressure can reach values as high as 1100 daN/cm² [1].

The recrystallisation pressure is influenced by porosity (dimension and distribution of pores), the water absorption and by temperature. Gypsum enlarges its volume in the presence of water; the destructive effect increasing linearly from one cycle to another (rain, freezing). Some examples of limestone buildings affected by gypsum are shown in Figure 4.



Figure 4. "Black crust" of gypsum and dust to the surface of some limestones: a) in the lower part the limestone is intensive affected by the "black crust"; b) limestone flakes under the gysum "black crust"



Figure 5. "Black crust": a) to the contact of the mortar and the limestone surface; b) rain water determine the hydratation and the crystalization of the gypsum, forming the "black crust"

2. Laboratory tests

Limestone degradation is stronger in the case of samples with high porosity, where water penetrates in larger amount and determines the fine (clay) particles in the matrix to be engaged in the dissolution of soluble particles (salts, carbonates, bioclastes) and their recrystallisation (salt, gypsum, calcite, dolomite), pores with large volume have a large surface area and chemical reactions are strong.

Limestones have often clastic or bioclastic content, and are prone to high chemical attack, salt-induced decay as well as severe and/or prolonged freezing.

In order to determine the physical properties of limestone it was used four samples having different porosity and rate of damages.

The density was determined according to STAS 6200/10-73 [11], the water absorption according to STAS 6200/ 12-73 [12] and the porosity and compactness according to STAS 7107/3-80 [13]. The results are presented in the table below.

Sample	Density	Water ab-	Porosity	Compactness
	p(g/cm)	a _i (%)	11 (70)	C (70)
а	2,26	5,33	26,70	73,3
b	1,65	16,72	54,57	45,43
С	2,23	2,32	5,53	94,47
d	2,24	3,52	13,85	86,15

Table 1. Physical characteristics of analyzed limestones

The petrographic features of studied limestones were evidenced in thin sections (Figure 6) using a Jenapol polarising microscope with transmitted light.

The thin sections shows that:

- sample **a** is an homogeneous bioclastic packstone with a lot of carbonate bioclasts and ooids, and lower content of quartz;
- sample b is a bioclastic grainstone-packstone, intensively weathered (see the thin sections Figure 6b- high porosity, maybe the soluble minerals were removed from the limestone before the present determination), being an heterogeneous limestone from mineralogical point of view (carbonate bioclasts, quartz, micas, calcite);
- sample **c** is an bioclastic packstone with carbonate cement, large ooliths and other bioclasts;
- sample **d** is an heterogeneous limestone, with bioclasts, large grains of quartz and micrograins of calcite.



Figure 6. Thin sections: a) Homogeneous bioclastic packstone (1-milliolids, benthic foraminifera; 2-ooids; 3- fragments of molluscs) b) Bioclastic grainstone-packstone (1-red algae; 2-bryozoa;3-benthic foraminifera; 4-secondary porosity,dissolution of the matrix) c) Bioclastic packstone(1-ooids; 2-fissurated ooids) d) Heterogeneous limestone (1-milliolids; 2-red algae; 3-calcite-lithoclast; 4- fragments of molluscs; 5-quartz-lithoclast)

Laboratory tests show that:

- samples a and c have a large content of carbonate (as bioclasts and calcite), a high density and lower water absorption but different porosity (a sample has a high and closed porosity);
- sample **b** has lower density and a higher porosity that influences the water absorption and dissolution of carbonates;
- sample **d** has high density, lower water absorption and a lower porosity.

From all the analyzed samples the most affected by environmental factors is the **b** sample due to the large open pores and large surfaces of reactions.

3. Conclusion

The decay of limestone is different from one sample to another one, because of the physical properties, mineralogical structure and chemical composition.

In the limestone with high porosity (thin section- \mathbf{b} sample) the water penetrates in large amount and determines the engagement of the fine grains (clay, quartz) of the matrix and the dissolution of soluble particles (salts, carbonates) or their recrystallisation (salt, gypsum, calcite, dolomite). In these ways the limestone becomes higly sensitive to water uptake and weathering effect is much more increased.

The chemical action of sulphate anions hastens limestone damages, though the differentiation regarding decay intensity concerns particular microstructural characteristics.

References

- 1. Duca V., *Bazele fizico-chimice și mineralogice ale petroarheometriei, Seria mineralogia aplicată*, Editura Arcadia Media, 2010.
- El Gohary M.A., *Investigations on limestone weathering of el tuba minaret el mehalla, egypt: a case study*, Conservation dept., Sohag University, Egypt, Mediterranean Archaeology and Archaeometry, Vol. 10, No. 1, pp. 61-79, 2010.
- Frattari A., Albatici R., Umiditatea in constructii, Proiect pilot No.HU 170003-2003, Formare Profesionala in Monitorizarea, Operarea si Intretinerea Cladirilor V E T – B O O M, Universitatea Tehnica din Cluj Napoca, 2005.
- 4. Frossel F., *Uscarea zidariilor si asanarea subsolurilor*, Editura Tehnica, Bucuresti, 2005.
- Graeme C., Study of Chemical consolidants, The winston Churchill memorial trust of Australia, 2000. http://www.churchilltrust.com.au/site_media/fellows/2000_Corney_Graem e.pdf
- Larbi J.A, Van Hees R.P.J, Naldini S., *Microscopic study of weathering of white flemish stone from the monumental Church of our Lady in Breda*, The Neterlands, TNO Building and Consttruction Research, Delft, The Netherlands (http://heronjournal.nl/48-3/5.pdf).
- 7. Mackenzie Fred T., *Carbonate mineralogy and geochemistry,* in Encyclopedia of Sediments and Sedimentary Rocks, G. V., Middleton, Encyclopedia of Earth Sciences Series, 2003.
- 8. Odgers D., Pinchin S. and all, *Investigations into decay mechanisms of magnesian limestone at chapter house, Howden minster,* Proc. 11th Int. Cong. on Deterioration and Conservation of Stone, Torun, J. Lukaszeqicz &

P. Niemcewicz, eds., Nicolaus Copernicus University Press, Vol 1, pp 211-221, 2008.

- 9. Torraca G., *Lectures on Materials Science for Architectural Conservation*, The Getty Conservation Institute, Los Angeles, 2009.
- 10. http://apmcj.anpm.ro
- 11. STAS 6200/10-73- Pietre naturale fasonate pentru construcții- Metode de încercări fizice, mecanice și mineralogice. Determinarea densității și greutății volumice
- 12. STAS 6200/12-73- Pietre naturale fasonate pentru construcții- Metode de încercări fizice, mecanice și mineralogice.Determinarea absorbției de apă și a cedării apei.
- 13. STAS 6200/13-80- Pietre naturale pentru construcții Determinarea compactitatii, porozitatii si a coeficientului de saturatie.

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