

Available online at www.sciencedirect.com



Procedia Earth and Planetary Science

Procedia Earth and Planetary Science 17 (2017) 316 - 319

15th Water-Rock Interaction International Symposium, WRI-15

A study of salt weathering cycles impact on limestones

Carlos Alves^{a,1}, Carlos Figueiredo^b, António Maurício^b

^aLandS/Lab2PT (UID/AUR/04509/2013; POCI-01-0145-FEDER-007528) and School of Sciences, University of Minho, Portugal ^bCERENA - Centro de Recursos Naturais e Ambiente (UID/ECI/04028/2013), Instituto Superior Técnico, University of Lisbon, Portugal

Abstract

Here are discussed results of salt weathering laboratory tests on specimens of three limestones, two grainstones (designated as Semi-rijo and Moca Creme) and a travertine, considering parameters related to an initial mass increasing phase and to mass differences between cycles in the mass decreasing phase. Results show a good ordinal correlation between final mass loss and maximum difference between cycles that differentiates the considered rock types.

© 2017 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license

(http://creativecommons.org/licenses/by-nc-nd/4.0/).

Peer-review under responsibility of the organizing committee of WRI-15

Keywords: limestones; grainstones; travertine; natural stone; built environment; accelerated salt weathering tests

1. Introduction

Salt weathering is, globally, a main erosive process affecting stony materials in the built environment (several examples can be found in¹). However, there are few laboratory studies regarding salt weathering along time. Among those are studies based on immersion in sodium sulphate solutions². These authors refer an initial mass increasing phase corresponding to salt intake, eventually followed by a second phase (which might not be present in some samples) that can be either of mass increase or decrease (resulting from salt intake and disintegration), followed by a third, clearly mass decreasing, phase. A study using synchrotron X-ray microtomography³ showed the accumulation of salt crystals in the pores along salt cycles, a result attributed to a continuous increase of salt ions in the pore space. In a previous work on the same specimens considered here⁴, it was referred that profiles of mass variation showed initially increasing mass up to a maximum mass and decreasing mass after this maximum mass. These authors⁴ computed two parameters related to the mass increase phase (mass increase after the first cycle and maximum mass increase), comparing the statistical distribution of these parameters in the studied rock types. These studies⁴ showed that, at the end of the tests, travertine specimens presented lower mass loss than those of the grainstone types

^{*} Corresponding author. Tel.: 351253604300. *E-mail address:* casaix@dct.uminho.pt

and that, among the grainstones, losses were higher in Moca Creme specimens. It was proposed⁴ that in the travertine specimens, presenting worst results in capillary imbibition tests, textural heterogeneities hindered the access of salt solutions to pore space, limiting the impact of salt weathering. Comparing Semi-rijo and Moca Creme, the presence in this last rock type of marked heterogeneities, such as bioclasts and veinlets, could explain the higher values of mass loss. Erosive patterns were also different, with travertine specimens showing marked heterogeneous patterns while grainstones specimens presented more homogeneous patterns that followed the specimens' contours. These differences were attributed to the size of dominant heterogeneous features in relation to the specimens' size⁵. Travertine specimens also showed⁴ lower values in the mass increase phase of the salt crystallization tests while there were not clear differences between the grainstone types. The average profiles of these two grainstone types showed a very similar (almost identical) mass increase phase and that the divergence occurs in the mass loss phase.

Using laboratory data from three limestones (two grainstones and a travertine), we attempt here to further our previous studies on parameters related to evolution along salt weathering cycles, both in the mass increasing and mass decreasing phase, and relate these results to mass loss at the end of the tests and to rock characteristics.

2. Materials and methods

The studied rocks were three Portuguese rocks, two grainstones (Semi-rijo and Moca Creme) and a travertine. The grainstones were described^{6,7} as fossiliferous pelmicrosparite/grainstone (Semi-rijo specimens) and as biopelintrasparite/grainstone (Moca Creme specimens). The studied travertine type shows⁸ a heterogeneous texture, sometimes very compact, others more friable and pulveriform, with a frequent presence of concentric cauliform vegetal forms. Following the European Standard for salt weathering⁹, cubic specimens of each limestone were subjected to salt crystallization tests using cycles of immersion in sodium sulphate solutions and drying. Results of the initial mass increase phase as well as the differences between cycles in the mass decreasing phase will be considered again here. All the plots were prepared with *Statistica* v. 11 software (Statsoft, Inc).

3. Results and discussion

Values of mass gain after the first cycle (MI1) were plotted (Fig. 1a) against the pore volume estimated from porosity measurements under atmospheric conditions, as well as lines corresponding to mass increase values expected from crystallization of thenardite (lower line) and mirabilite (upper line), lines that were defined from the pore volume and the characteristics of the salt solutions (density and salt content). In the figures, all continuous variables were plotted on a logarithm scale, as this allows a ratio comparison It can be seen that mass gains after the first cycle do not relate directly to the pore volume estimations, being higher in the grainstones (in some cases above the expected value from mirabilite crystallization) and lower in the travertine specimens (most results are below the mass gain expected from thenardite crystallization). This can be explained by heterogeneity in travertine specimens affecting (and limiting) the access of salt solutions to pore space. As referred to above, mass keeps increasing up to a maximum value (MMI). Values of MMI/MI1 were plotted against the cycle number where MMI is achieved (Fig. 1b), showing that this ratio is higher in the grainstones that also show a longer (more cycles) mass increase phase. Dispersion of MMI/MI1 values is, proportionally, similar on the three rock types. The mass loss at the end of the tests (FML) was plotted (Figure 2a) against the maximum mass increase (MMI, that can be considered an indication of salt load). While grainstones' specimens presented higher salt mass increase and higher mass loss than travertine specimens, the two grainstones types present similar salt loads but different final mass loss values. We conjectured that another approach to assess salt load could be to transform the mass increase in salt volume and compare this value to the rock pore volume (salt volume estimations were based on density values presented in¹⁰). As shown in Fig. 2b, there is no clear correlation of this parameter with final mass loss but in relation to values of the ratio between salt volume and pore volume one can highlight that: i) they are of the same order of magnitude of final mass loss; ii) values for travertine specimens do not exceed 5%, corroborating the idea that there is a limited access of salt solutions to the travertine pore space (considering the crystallization of mirabilite this ratio will not exceed 10%). The specimen's mass during the mass decreasing phase could be affected by the initial mass increase. So, following a proposal of using the differential of mass evolution², final result (mass loss) values of salt weathering tests were plotted against the median of differences between successive cycles in the decreasing phase (Fig. 3a).

While there is a certain trend for correlation, separation between grainstones types is rather weak. Better results are obtained considering the maximum (absolute) value of mass loss between successive cycles (Fig. 3b) as this parameter gives the same petrological ordering (i.e. in terms of stone type) observed in the mass loss at the end of the tests.

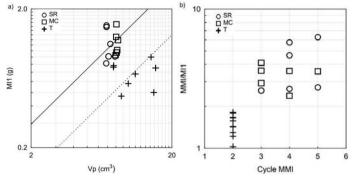


Fig. 1. a) Plot of mass increase after first salt cycle (MI1) against pore volume (Vp); (b) plot of ratio between maximum mass increase and mass increase after the first cycle (MMI/MI1) against cycle number where MMI is achieved.

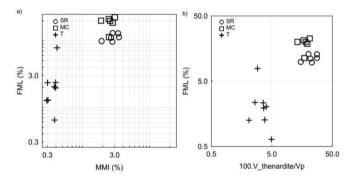


Fig. 2. Plot of final mass loss (FML) against (a) maximum mass increase (MMI); (b) proportion of salt volume (assuming thenardite crystallization) over pore volume (100.V_thenardite/Vp).

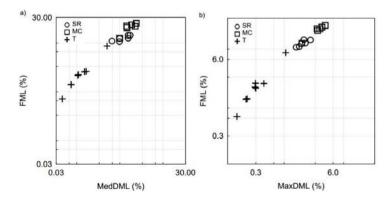


Fig. 3. Plot of the final mass loss (FML) against (a) median of differential mass loss (MedDML); (b) maximum differential mass loss (MaxDML).

4. Final considerations

All the considered specimens (travertine and the grainstone types, Semi-rijo and Moca Creme) showed mass increase after the first cycle of imbibition in salt solution and drying. This initial mass increase (MI1) is not related to available pore volume in a simple way, being affected by the accessibility of the pore space. In travertine specimens, that had showed worst results in capillary imbibition tests, maximum salt load is achieved sooner and both values of salt load in relation to the rock pore volume and mass loss at the end of the salt weathering tests are clearly lower. This supports the hypothesis that, in this rock, salt solutions flow is limited to some specimens' portions as the pore space is more discontinuous and hence, afterwards, during salt crystallisation, these are the only ones affected by salt crystallization (this also explains their heterogeneous decay patterns). In the grainstones, salt solutions have a more widespread and uniform access to the pore space, which also implies higher salt load (similar in Semi-rijo and Moca Creme). The final, cumulative, mass loss correlates well with the maximum difference between successive cycles and is higher in Moca Creme specimens, corroborating the previously proposed hypothesis regarding the effect of coarser textural features of this rock type.

Acknowledgements

The Lab2PT, Landscape, Heritage and Territory Laboratory (UID/ECI/04028/2013) of the University of Minho and the CERENA - Centro de Recursos Naturais e Ambiente (UID/ECI/04028/2013) of the Instituto Superior Técnico, University of Lisbon are supported by the FCT - Fundação para a Ciência e Tecnologia (Portugal), with Portuguese funds and funds from the European Union (FEDER, Programa Operacional Factores de Competitividade – COMPETE 2020 – Programa Operacional Competitividade e Internacionalização, POCI, POCI-01-0145-FEDER-007528). The experimental data here discussed were obtained in the context of the Project PORENET (POCTI/CTA/44940/2002) also funded by the FCT. Acknowledgments also to Eng. Teresa Luís, Eng. Sónia Pereira, and Enterprise Mármores Galrão for the rock blocks.

References

1. Goudie A, Viles HA. Salt weathering hazards. Chichester ; New York: Wiley, 1997.

2. Angeli M, Bigas JP, Benavente D, Menéndez B, Hébert R, David C. Salt crystallization in pores: quantification and estimation of damage. *Environ Geol* 2007;**52**:205-213.

3. Derluyn H, Dewanckele J, Boone MN, Cnudde V, Derome D, Carmeliet J. Crystallization of hydrated and anhydrous salts in porous limestone resolved by synchrotron X-ray microtomography. *Nucl Instrum Methods Phys Res Section B: Beam Interact Mater Atoms* 2014;**324**:102–112.

4. Alves C, Figueiredo C, Sequeira Braga MA, Maurício A, Aires-Barros L. Limestone under salt decay tests: assessment of pore network-dependent durability predictors. *Environ Earth Sci* 2011;63:1511-1527.

5. Alves C, Figueiredo C, Maurício A, Aires-Barros L. Susceptibility of Limestone Petrographic Features to Salt Weathering: A Scanning Electron Microscopy Study. *Microsc Microana* 2013;**19(05)**:1231–1240.

6. Figueiredo C, Folha R, Mauricio A, Alves C, Aires-Barros L. Contribution to the technological characterization of two widely used Portuguese dimension stones: the 'Semi-rijo' and 'Moca Creme' stones. In: Prikryl R, Török Á (eds.) *Natural Stone Resources for Historical Monuments*, Special Publications 333, Geological Society, London, 2010, pp 153-163.

7. Figueiredo C, Folha R, Mauricio A, Alves C, Aires-Barros L. Pore structure and durability of Portuguese limestones: a case study. In: Smith J, Gómez-Heras M., Viles HA, Cassar J (eds) *Limestone in the Built Environment:Present-Day Challenges for the Preservation of the Past*, Special Publications 331, Geological Society of London, 2010, pp 157-169.

8. Romariz C. Estudo Geológico e Petrográfico da Área tifónica de Soure. Comunicações dos Serviços Geológicos de Portugal, Tomo XLIV, 1960. In Portuguese.

9. CEN/TC 246 - Natural stones. EN 12370:1999. Natural stone test methods - Determination of resistance to salt crystallisation. CEN-CENELEC Management Centre: Brussels, 1999.

10. Downs RT, Hall-Wallace M. The American Mineralogist Crystal Structure Database. Am Mineral 2003;88:247-250.