



## 18<sup>th</sup> century Portuguese tiles: characterization and reproduction study of Ca-rich biscuits

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*SUMMARY: Majolica tiles from the 17<sup>th</sup>-18<sup>th</sup> centuries make up one of the most important art heritages of Portugal. Their characterization and gains in knowledge through their reproduction are important to obtain information about their production methods, raw materials used, origin attribution and to contribute to studies in conservation and development of treatments.*

*A group of Lisbon tiles from the late 17th to 18th centuries has been previously characterized and the biscuits now tentatively reproduced. Special attention was given to the effect of firing temperature and Ca compounds content on the final replica properties such as water absorption, porosity, water and thermal expansibilities, mechanical strength, chemical composition and mineralogy. Correlation models between the Ca compounds content and firing temperature were obtained for the previous properties. Replicas similar on those properties considered relevant were obtained that can be used in studies in conservation and in interventions.*

*KEY-WORDS: Ceramic biscuit, historic tiles, calcitic clay, reproduction, replica*



## INTRODUCTION

Reference ceramic materials with property similar characteristics to the original historic materials are necessary in research in conservation where the simulation of decay or the comparative study of intervention treatments is necessary. Such need stems from the impossibility of using large quantities of original materials of heritage value, azulejos in this case. Technical replicas are also useful as a compatibility assurance when doing tile panels conservation treatments [1].

A search was previously performed on commercially available biscuit tiles produced as tentative replicas of ancient tiles (azulejos) ceramic bodies, leading to the conclusion that nowadays available biscuits and pastes were produced with Ca-poor clays different from the Ca-rich compositions used formerly to produce azulejos. This implies a chemical and mineralogical dissimilarity between the available semi-manufactured replicas and the historic tiles [2,3,4,5]. However, those biscuits presented in many cases similar physical properties such as porosity, thermal and hydric expansibilities which, in the absence of biscuits mineralogically more similar, could still be used on research in conservation treatments if the results were validated in actual historic azulejos. But a ceramic reference biscuit presenting higher similarity in respect to its chemical and mineralogical composition, besides the physical characteristics, would be preferred to perform such studies.

In order to understand the effect of calcite addition to the clay, to form Ca-rich pastes with similar compositions to those originally used, on the properties of the final biscuits a systematic study was performed in which the content of calcite in the paste and the firing temperature were varied. In order to further simulate the range of porosities observed in historic tiles organic matter was also added to selected pastes. In this paper the obtained results are presented and discussed.

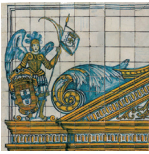
## METHODS

A group of seven Portuguese tiles manufactured from the early to the late 18<sup>th</sup> century, likely by Lisbon workshops, have been previously chemically, mineralogically and physically characterized [6] and their biscuit properties tentatively reproduced.

Untreated clay (TG-21 supplied by *Sorgila Lda.*) was mixed systematically with varying amounts of calcite in order to produce 0, 25, 35 and 45 % (wt) CaO containing pastes. The obtained pastes were fired at 850, 950 and 1050 °C obtaining 12 resulting biscuit typologies plus some replicates composing a full-factorial design experimental plan.

The resulting biscuits have been studied in what respects their chemical and mineralogical composition by SEM-EDS and XRD. Their physical properties have been determined by colorimetry, hydrostatic weighing, mercury intrusion porosimetry, water absorption by capillarity, flexural strength as well as the water and thermal expansibilities. The physical properties obtained due to % CaO and firing temperature variation were modelled using *Design-Expert Software vs. 9.*

Increased amounts of organic matter were added to a selected paste made up of clay and calcite in order to impart higher and different porosity ranges.



## SYNOPSIS OF THE RESULTS

As expected, the addition of calcite to the clay and the increase on firing temperature has influenced the final physical and mechanical biscuit properties evaluated. A decrease in the reddish biscuit colour towards a more common buff one was observed with increase of CaO content and firing temperature (Figure 1), as well as a decrease in the water expansibility and a higher flexural strength with the increase of the firing temperature.

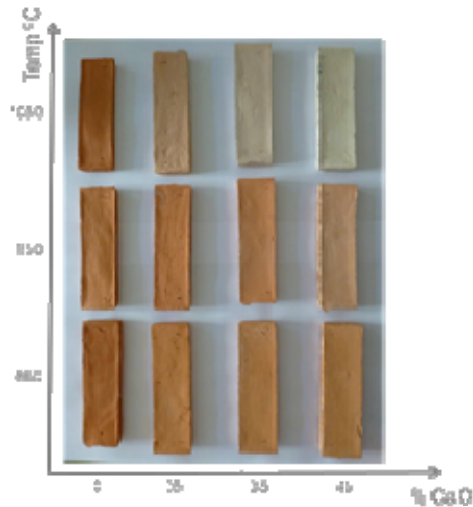


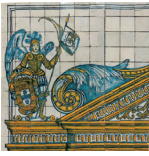
Figure 1 - Colour variations in the ceramic biscuits obtained with various CaO contents and firing temperatures.

For most of the physical properties determined, a statistically significant model was obtained which correlated the results to the % content of CaO and firing temperatures. The setting of a desirability function and the treatment of the models previously obtained allowed selecting an optimal composition-firing temperature range which produces ceramic biscuits with the physical properties most similar to the properties of historic tiles previously determined [5].

The addition of organic matter to the pastes composition allowed obtaining a straight correlation between the amount of organic matter added and the final open porosity, permitting a simulation of biscuits porosity in the range of 35 to > 55%. These samples with an increased porosity can be very useful in conservation studies where the simulation of decayed ceramic tile matrixes is needed.

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## Bibliographic references

- <sup>1</sup> COSTA, M; Cachim, P; Coroado, J. & Velosa, A.L. - *Technical replicas of Portuguese ceramic tile bodies produced in the Oporto region in the late nineteenth to early twentieth centuries*, Studies in Conservation, 2015.
- <sup>2</sup> MUSACCHI, J. - *Conservation of historic Portuguese tile: Adhesives for outdoor exposure*, Master Thesis, Bologna University, Italy, academic year 2011-2012.
- <sup>3</sup> TRINDADE, M.J; Dias, M.I; Coroado, J. & Rocha, F. - *Mineralogical transformations of calcareous rich clays with firing: A comparative study between calcite and dolomite rich clays from Algarve*, Portugal, Applied Clay Science, 42, 2009, 345-355.
- <sup>4</sup> RICCARDI M.P; Messiga, B. & Duminuco, P. - *An approach to the Dynamics of clay firing*, Applied Clay Science, 15, 1999, 393-409.
- <sup>5</sup> CULTRONE G; Rodriguez-Navarro, C; Sebastian, E; Cazalla, O. & De la Torre, M.J. - *Carbonate and Silicate phase reactions during ceramic firing*, European Journal of Mineralogy, 12, 2001, 621-634.
- <sup>6</sup> PEREIRA, S; Mimoso, J.M. & Santos-Silva, A. - *Physical-chemical characterization of historic Portuguese tiles*, Relatório LNEC 23/2011, Lisbon, LNEC, 2011.