Restoration of semi-industrial glazed ceramic tiles by re-firing

Antonina Chaban
University of Bologna, Italy, antonina.chaban@gmail.com
Silvia R. M. Pereira
Laboratório Nacional de Engenharia Civil, Lisbon, Portugal, spereira@lnec.pt
Maria de Lurdes Esteves
Museu Nacional do Azulejo, Lisbon, Portugal, mnazulejo.lurdesesteves@imc-ip.pt
Fausto Peddis
University of Bologna, Italy, fausto.peddis@unibo.it
João Manuel Mimoso
Laboratório Nacional de Engenharia Civil, Lisbon, Portugal, jmimoso@lnec.pt

SUMMARY: Semi-industrial glazed ceramic tiles lining urban façades represent a rich heritage asset of Portuguese cities and in particular of Lisbon. However, still a sizeable part of them is being continuously lost. Whenever the façade tiles are decayed, they are usually merely removed and replaced by newly manufactured ones.
Following preliminary tests done at LNEC in 2012, we introduce in this communication re-firing as an alternative to simple disposal of damaged original tiles. We assess the technique as a technological option for the restoration of crazed and spalled tiles. The re-firings are applied at different heatworks and temperatures and the effects of all tests are studied by visual, microscopic observation and through the glaze resistance to a pull-off. The effect of continuous serviceability of the re-fired tiles is assessed through accelerated ageing tests. The domain of application of the technique and the shortcomings detected are presented and discussed in this communication.
Dwelling on a new ground, we present the initial results on which further research in this field can be based.

KEY-WORDS: azulejos; façade tiles; restoration; re-firing of ceramics; acquired calcium carbonate in ceramics

1. INTRODUCTION

Since the 16th century azulejos (ceramic tiles) are closely related with the life and culture of the Portuguese. There is no other country in the world where we can admire such an abundant heritage of azulejos as in Lisbon, Oporto, Evora and many other Portuguese towns and even small villages. They are used wherever large areas are available, in the interiors of churches and palaces, cloisters, halls, staircase walls of multi-storey buildings and, since the second quarter of the 19th century, covering whole urban façades [1]. The use of azulejos in Portugal is arguably its most original contribution to the artistic heritage of Europe and so they represent a valuable asset.

The historical individually painted tiles are easily conceived as art creation and so different techniques are developed and applied to their conservation and restoration [2]. However, the semi-industrial tiles are still considered expendable and in towns such as Lisbon a sizeable part is lost every year through decay and neglect [3].

The township of Ovar tries to restore the individual tiles of its urban façades [4, 5], but with few exceptions whenever buildings are restored, decayed azulejos are usually removed and replaced by newly manufactured tiles, often with low aesthetic quality and of inferior quality as well. The original tiles removed from the walls are often seen in the dump containers, simply thrown away. In some cases they may be packed and stored by the town authorities for future reference and in such cases they may one day be given new life.

The individually painted panels represent integrated art that complements Architecture and thus hold a set of values (both in themselves and through their integration) that preclude the impairment of their historical value through re-firing, unless there were no other means to preserve the image [6]. The façade tiles, unlike the historical azulejo panels, are repeating units deriving from a semi-industrial process, all similar and holding the same intrinsic values. Because during the process of urban restorations the damaged tiles are simply thrown away, any technique allowing their continued serviceability would constitute a better option, even if some values such as the historical record of the original manufacturing technique were impaired or even lost in the process.

2. PREVIOUS STUDIES AND OBJECTIVES OF THE RESEARCH

Three years ago LNEC found out as a by-product of another research that in at least some cases crazing could be mended and a decaying adhesion could eventually be restored by re-firing the tiles [7] and proposed to dwell into the possibility of restoring façade tiles by re-firing them.

The tests were done at the Museu Nacional do Azulejo (National Azulejo Museum, in Lisbon) in 2012 on three historical hand-painted azulejos of the 17th and 18th centuries and on a single semi-industrial (early 20th century) tile. Tiles were cut in four probes; one was kept in its original condition and the other parts were fired at 890°C, 990° and 1100°C with a heating rate of 240°C per hour and a stage of 20 minutes at the maximum temperature. The first tests showed that at least in some cases crazing could be reversed and the glaze to biscuit adhesion was not seen to be impaired. Actually the pull-off strength could potentially be increased by re-firing to a sufficiently high temperature [7]. The subject has been pursued within the present research project aiming at developing a feasible restoration method usable for semi-industrial patterned tiles. The research was pursued at LNEC in collaboration with the University of Bologna originating a MSc dissertation "Restoration of semi-industrial glazed ceramic tiles by re-firing", defended in Italy in March 2015 [8].

3. RE-FIRINGS

35 semi-industrial samples were selected, representative in terms of the period (2nd half of the 19th century to early 20th century) and decay forms (crazing and glaze loss). They were tentatively dated according to their technical and stylistic features. The industrial provenance of several samples was known and they were manufactured by Fábrica Roseira, one of the first and main protagonists of façade tiles production in Lisbon [9]. The residuals of mortar on the tiles were removed manually as a possible source of gaseous emissions during the re-firing; the tiles were cleaned and desalinated according to the standard procedure of immersion in de-ionized water [10]. The whole tiles and larger fragments were first cut in four or five test items, some being subsequently re-divided into smaller pieces for comparative re-firings, ageing procedures or characterization purposes.

3.1 Methodology outline

The re-firing technique was applied at several heatworks and maximum temperatures, and characterized in terms of its efficacy addressing the following problems: i) glaze crazing; ii) insufficient glaze to biscuit adhesion; and iii) reintegration of lacunae in areas where the glaze had been lost.

At the beginning we planned to use only simple cycles made up of continuous heating and cooling ramps at constant rates which we call here *single-stage re-firings*. They have been applied on different samples to 890, 930, 950, 990 and 1100°C with a ROHDE KE-150 L kiln (front loader, maximum temperature 1280°C). In all cases a heating ramp of 240º/h was used because it is the standard heating rate used by the Museu Nacional do Azulejo and it is the fastest recommended by their long experience on the glazing of reproductions.

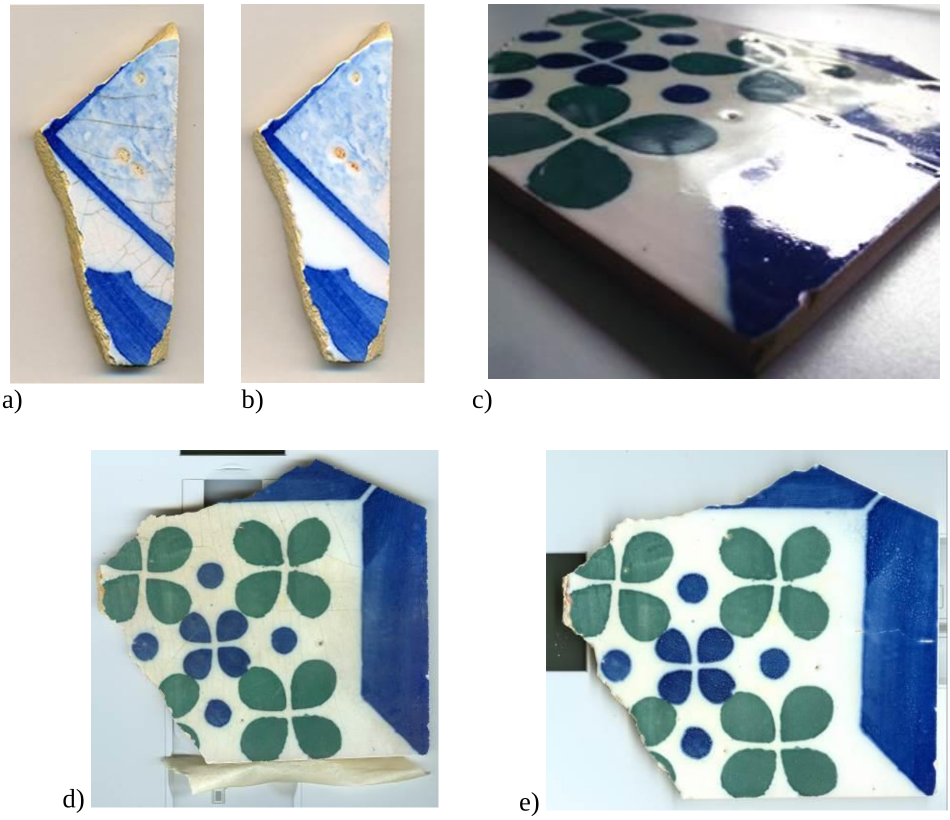
3.2 Single stage re-firing

The *single stage re-firing* obliterated the crazing, restored the glaze whiteness and shine (Figure 1) and showed good promise in terms of lacunae restoration for most samples. But in three of 35 tiles it failed. In these cases a restoration was not achieved due to bubbles protruding from the glaze surface or extensive "orange skin" on the surface.

At the same time, all the samples showed an increase in porosity when re-fired at the lower range of temperatures but a decrease in open porosity in all cases when re-fired at 1100°C. The results of mercury intrusion porosimetry have showed a slight increase in pore size in the samples re-fired at 890 and 950°C (Figure 2).

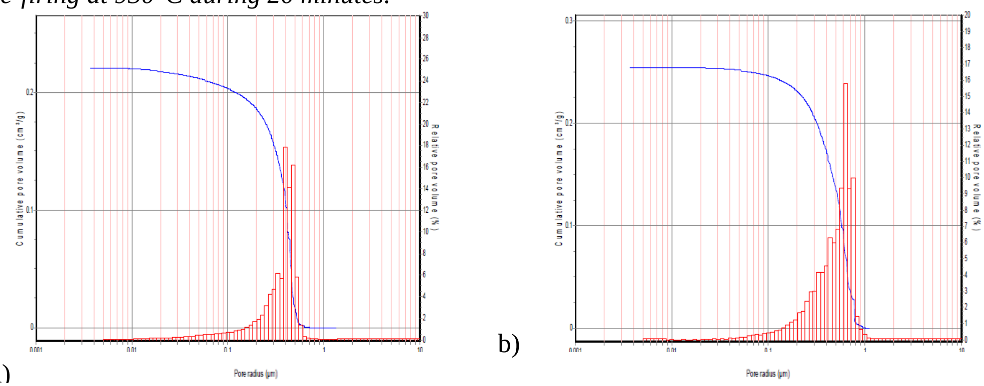
The glaze to biscuit adhesion did not show to worsen after re-firings and in two cases small pieces of detached glaze were verified to have adhered after re-firing in a way that they could not be separated with the nail. In no case did a pull-off test detect any evident impairment of the glaze to biscuit adherence (Figure 4) but it made evident that the cohesion of the biscuit decreased on the firings at lower temperatures but increased in all cases at 1100ºC.

The micro-hardness Knoop tests and nano-indentation tests showed that there was no systematic alteration and no significant changes in the glaze mechanical properties due to re-firing [8].



a) b) c) d) e)

Figure 1. Visual observation of single-stage re-firing results: *a) and d) before re-firing; b) after re-firing at 890°C during 3 hours; c) glossy glaze surface after re-firing e) after re-firing at 930°C during 20 minutes.*



a) b)

Figure 2. Pore size distribution diagrams: *a) before re-firing, peak ø 0.3-0.4 μm; b) after re-firing at 950°C during 40 minutes, peak ø 0.6-0.7 μm.*

The microscopic observation of the glaze (Figure 3) in the studied samples has shown that crazing cracks had been effectively sealed through re-firing eventually leaving scar-like marks. The number of bubbles seen in the glaze also tended to decrease, through confluence or elimination at the surface (Figure 3).

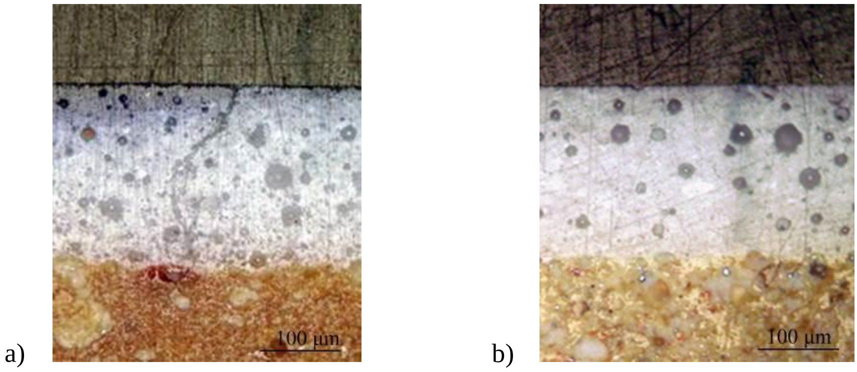


Figure 3. OM observations of single-stage re-firings*: a) before re-firing; b) after re-firing at 950°C during 20 minutes.*

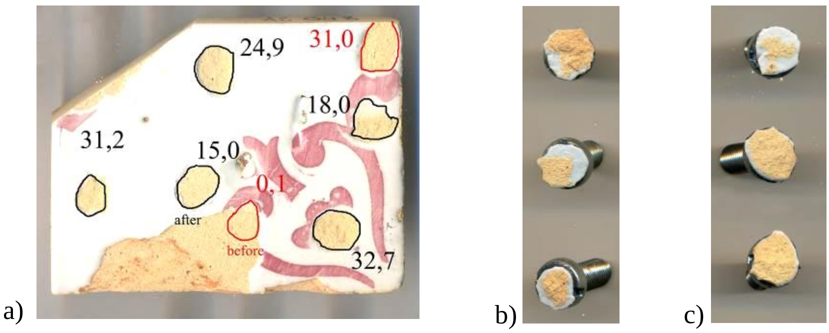


Figure 4. Pull off tests: *a) ultimate force results before (red) and after re-firing (kN); b) fracture in not re-fired condition; c) facture after re-firing at 950°C during 40 minutes.*

After these observations and tests, we addressed the impairment of the glaze surface seen in some cases. The fact that bubbling through the glaze now compromised the aesthetics of the decoration in tiles that were originally fired at similar or higher temperatures, suggested that whatever was causing this problem had been acquired during the service lifetime of the tile. Since free water and organic material are lost or consumed at lower temperatures than that at which the glaze softens [11], a de-carbonation process was suspected. This hypothesis led to a study of the calcite content of the samples.

Although the biscuits of recently fired azulejos cannot have a sizeable content in carbonates, in aged units calcite may eventually have been formed through re-carbonation of lime (either acquired from the walls or remaining in the biscuit after the original firing) [11]. And indeed, the presence of calcite was confirmed by loss on ignition tests performed at LNEC (see Table 1) confirmed by X-ray diffraction analysis performed at the University of Bologna [8].

Table 1. Loss on ignition results in tile AC 26

Sample	Re-firing	Loss of CO2 (500-900ºC)*		CaCO3 (%)
		(g)	(%)	
AC 26a	**None**	0,032	3,21	**7,30**
AC 26a	**Single stage firing** *990°C for 5 minutes*	0,0015	0,19	**0,43**
AC 26c2	**Double stage firing** *700°C during 3 hours at 950°C for 5 minutes*	0,0015	0,15	**0,34**

* assuming that all losses in this temperature range are due to release of CO2

An analysis by SEM-EDS of a re-fired sample identified lime or calcite deposited in the hollows accessible to solutes circulating in the walls and biscuits. Upon firing the calcite is transformed into lime or combined e.g. with silica to form wollastonite or with aluminosilicates to form e.g. gehlenite, releasing carbon dioxide in the process (Figure 5).

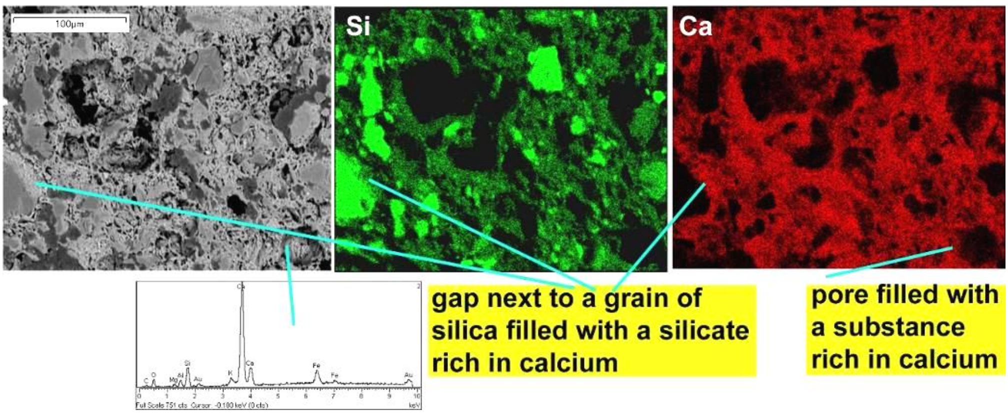


Figure 5. SEM observations of a re-fired sample.

The increase in mass by accelerated carbonation testing (at LNEC) confirmed that: i) there is lime present in the samples indicating that not all calcium was combined in species such as gehlenite and wollastonite during the original firing, or that lime was acquired afterwards from the mortars; and ii) that lime is accessible and readily carbonates, re-forming calcite.

3.4 Double stage re-firings

To address the unexpected problem we decided to replicate in part the manufacture process. We introduced *double-stage re-firings* and evaluated their effect on different samples. The heatwork relevant for the re-firing of the glaze (i.e. above its softening temperature) is the same both in single and double stage re-firings. The difference is that double-stage re-firing processes foresee extra time for calcite transformations inside the ceramic body before the softening of the glaze. In practice it means that the heating ramp is stopped and maintained for a period at the temperature point when the carbonates decomposition has already started but the glaze has still not melted (600-700°C).

The method worked well and the bubbling problem was successfully solved (Figure 6). The further tests were aimed at finding the minimal duration and optimal temperature to let the carbonates decompose and the carbon dioxide escape from the ceramic body. Heating ramps of 200°C/h and 240°C/h were tested, as well as the effect of pre-firings on 21 samples at 550, 600, 650 and 700ºC during 1-4 hours. The maximum temperatures evaluated in double-stage re-firings were 890, 950 and 990°C. However, it was still not possible to avoid completely the appearance of "orange skin" on the surface of one tile. We can assume that this anomalous result is caused by the glaze softening at a lower temperature than in the other tiles so that during the de-carbonation phase the gas already starts bubbling through the glaze.

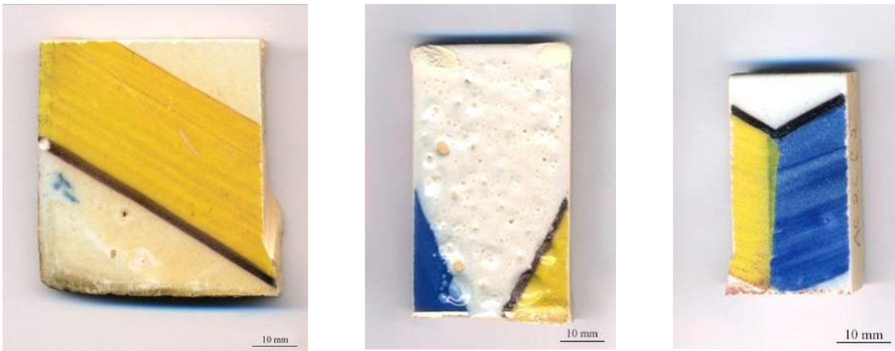


Figure 6. Visual observation of double-stage re-firing results: *a) not re-fired; b) single-stage refiring (990°C 5 minutes); c) double-stage re-firing*

4. AGEING TESTS

To evaluate the future performance of tiles restored by re-firing, two types of accelerated ageing tests were performed. The tiles were aged artificially by boiling in water according to the general lines of the EN155 Standard (maximum moisture expansion stress applied) and by exposure to a NaOH solution at 60°C during 30 days. Both ageing tests have shown that: i) the tests used are effective in the sense that they cause decay; ii) The re-fired samples followed the same ageing trend as their un-refired counterparts.

The re-firing treatment did not influence in any noticeable systematic manner the degree of pull-off resistance after ageing in boiling water. More revealing: the boiling in water caused in some cases new crazing but this did not usually coincide with the original crazing, meaning that the re-firing did reverse the fissures in a way that the scars do not constitute preferential propagation paths to new crazing phenomena (Figure 7).

a) b)

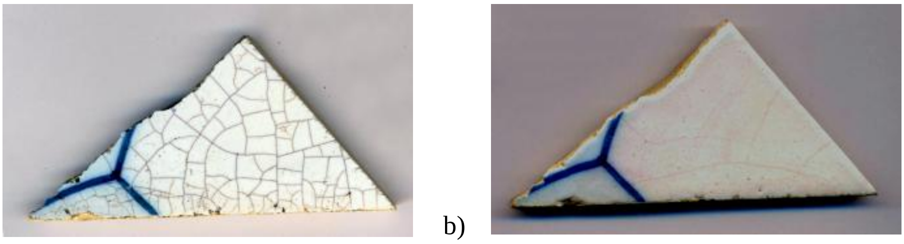


Figure 7. Comparison of crazing pattern: *a) not re-fired; b) re-fired and aged in boiling water- crazing highlighted with red ink*

5. APPLICATION OF THE TECHNIQUE TO FULL RESTORATION OF TILES

The technique has been applied and evaluated as a technological option for full restoration of spalled tiles (Figure 8). The lacunae in 8 spalled tiles have been reintegrated with new glaze CE VTR- 81 (manufactured by Ferro S.A. and widely used nowadays in tiles production), painted and subsequently re-fired. The double-stage firing at 650°C for 3 hours and then 890°C for 45 minutes proved efficacious and 890°C is likely inferior to the temperature at which the biscuit has been originally fired [11] and should not lead to the formation of new chemical species in the ceramic body.

Small patches of minimal orange skin were occasionally reported but they did not led to unacceptable results. However, one sample returned completely unexpected results since the new glaze did not adhere to the biscuit and the original glaze now curled at the edges (Figure 8f). The problem in this case is not related to calcite decomposition during the firing and has not been explained so-far.

The most relevant problem that this project had to address was the fact that the ceramic body of an old tile removed from a wall now contains non-original/contaminant chemical species that have been accumulated with time in the porous network or products of alteration that release gases upon re-firing. The understanding of the cause of the bubbling and the development of a technique to overcome this obstacle were achieved through research.

Each case is a case in itself and although a receipt was developed that may be applied successfully to most cases, there was a definite failure. It is recommended that, if possible, preliminary tests and trials should be done to determine the content in carbonates of the samples and, in all cases, preliminary firings be run to check the response of the azulejos to different firing cycles so as to determine the most appropriate and efficient one.

a) before restoration;

b) after restoration by re-firing;

c) before restoration;

d) after restoration by re-firing;

Figure 8. Application of double-stage re-glazing and re-firing technique to the restoration of spalled tiles

e) before restoration; *f) after restoration by re-firing*

Figure 8. Application of double-stage re-glazing and re-firing technique to the restoration of spalled tiles

Acknowledgements

FCT funding support is acknowledged through the project CerAzul (PTDC/CTM-CER/119085/2010).

LNEC supported the participation of João Manuel Mimoso, under Project 0202/111/19014 of the Plan for Research and Innovation for 2013-2020.

Bibliographic references

[1] BARROS, V.A..J & Almasqué, I. - Azulejos de fachada em Lisboa, Câmara Municipal de Lisboa, Lisbon, 1989;

[2] PEREIRA, S; Esteves, L; Mendes, M.T; Musacchi, J; Delgado Rodrigues, J & Mimoso, J.M. *CerAzul: Assessment and development of materials and techniques for the conservation of historic azulejos*, In Azulejar 2012, Aveiro, 2012;

[3] MIMOSO, J.M; Pereira, S; Esteves, L & Santos Silva, A. - *A tour of façade azulejos decay in Lisbon*, in Proc. Int. Congress Azulejar, Aveiro, Portugal, Oct. 10-11, 2012;

[4] MOURA FERREIRA, I. - *Azulejos tradicionais de fachada em Ovar: contributos para uma metodologia de conservação e restauro*, Câmara Municipal de Ovar, Portugal, 2009;

[5] RIBEIRO, L; Ferreira, L.M; Coroado, J. & Velosa, A.L. (2012) - *Conservación y restauración del azulejo de Ovar – metodología para una intervención sostenible*, In Qualicer 2012, Castellón, Spain, 2012;

[6] MIMOSO, J.M. - *Cesare Brandi's "Theory of Restoration" and azulejos*, in Proc. Int. Sem. Conservation of Glazed Tiles, Lisbon, LNEC April 15-16, 2009;

[7] MIMOSO, J.M; Pereira, S. & Esteves, L. - *A matter of strength - measuring the glaze/biscuit adherence in Portuguese azulejos*, in Proc. Int. Congress Azulejar, Aveiro, Portugal, Oct. 10-11, 2012;

[8] CHABAN, A. - *Restoration of semi-industrial glazed ceramic tiles by re-firing*, Master's thesis Dissertation, discussed at the University of Bologna, School of Sciences, March 19, 2015;

9 MIMOSO, J.M. - *New stuff about old stuff: the azulejos of the Roseira Factory*, lecture given on Jan 14, 2015 at the ARTIS Institute of the University of Lisbon, https://blogazlab.wordpress.com/2014/12/19/coisas-novas-acerca-de-coisas-velhas-os-azulejos-de-fachada-da-fabrica-roseira-de-lisboa/;

[10] Fundação Ricardo do Espírito Santo Silva, *Festa barroca a azul e branco: exposição - conservação e restauro*, Lisbon: FRESS, 2003;

[11] PEREIRA, S; Mimoso, J.M & Santos Silva, A. - *Physical-chemical characterization of historic Portuguese tiles*, Relatório LNEC 23/2011, Lisbon, LNEC, 2011.