PRODUCTION TECHNOLOGY AND TECHNO-HISTORICAL VALUE IN FAIENCE *AZULEJOS*

João Manuel Mimoso[1], Lurdes Esteves[2,1]

[1] Laboratório Nacional de Engenharia Civil (LNEC), Av. do Brasil 101, 1700-066 Lisboa, Portugal, jmimoso@lnec.pt

[2] Museu Nacional do Azulejo, Rua da Madre de Deus, 4, 1900-312 Lisboa, Portugal, mesteves@mnazulejo.dgpc.pt

ABSTRACT

Aloïs Riegl in *The Modern Cult of Monuments*, originally published in 1903, was one of the first to ascribe a historical value to the results of a technology when he stated that even a torn-off slip of paper with a short unimportant note contains historical value for the development of paper manufacturing, script and writing materials.

Glazed ceramic tiles (*azulejos* in Portuguese) are widely appreciated and studied for their artistic content. Their historical value is dully recognized but research deals mostly with the painting, the use of colour, the subjects or designs depicted in historiated or pattern panels and the purpose of their use over time. There is however an important historical value in their technology.

The present text makes an overview of the pre-industrial technology of tile-making and offers some examples of how the historical content in that technology can be extracted and interpreted.

Keywords: Azulejo / Tile-making technology / Historical value in technology

1 INTRODUCTION

Aloïs Riegl in *The Modern Cult of Monuments*, originally published in 1903, was one of the first to ascribe a historical value to the results of a technology in the sentence: *[…] every historical monument is also a monument of art, since even such a subordinate monument as a torn-off slip of paper with a short unimportant note contains, along with its historical value for the development of paper manufacturing, script, writing materials, et cetera, a whole series of artistic elements: the outward appearance of the slip of paper, the shape of the letters, and the manner of its composition.* [1]

Glazed ceramic tiles (*azulejos* in Portuguese) are widely appreciated and studied for their artistic content. Their historical value is dully recognized but research deals mostly with the painting, the use of colour, the designs, the subjects depicted in historiated panels and the purpose of their use over time. There is however an important historical value in their technology, which we may call the *techno-historical value*. Azulejos were manufactured by the faïence (or majolica) technology, originated in the Middle East in medieval times and seemingly introduced to Europe through the Islamic kingdoms of Iberia. Majolica was perfected in Italy in the 15th century and exported with emigrant shop-masters to Spain and Antwerp in the early 16th century. Of these the establishment of Guido di Savino from Castel Durante in Antwerp (where he took the name *Guido Andries*) around 1508 [2] is particularly relevant because from his workshop irradiated, directly or indirectly, technological knowledge to several countries likely including Portugal [2, 3].

The present paper makes a quick overview of the pre-industrial technology of tile-making used since the Renaissance until the first half of the 19th century and shows some examples of how the techno-historical value can be extracted and interpreted. The results may later be used e.g. for provenance studies.

The study of the technology used several sources chronologically dated from *Li Tre Libri dell'Arte del Vasaio* written by Cipriano Piccolpasso in the second half of the 16th century [4], to *Ceramica Portugueza Moderna* (Modern Portuguese Ceramics) by Charles Lepierre, published in 1899 [5]. The reference to Piccolpasso is relevant because the improved technology that spread throughout Europe in the Renaissance originated in Italy.

The French treatise *L'Art de Fabriquer la Faïence Recouverte d'un Émail Opaque Blanc et Coloré* by F. Bastenaire-Daudenart was also consulted [6]. It was published in Paris in 1828, but the experience behind it was acquired by its author in the previous decades, when he had directed a factory in Saint-Amand-Les-Eaux, originally founded in 1705.

Finally the documentation of the Real Fábrica do Rato (RFR) was consulted [7]. In the last third of the 18th century it was the most technologically advanced manufacturer of faïence, including azulejos, in Portugal.

The production of azulejos involved many activities, some of them remarkably complex. The main manufacturing challenge was the obtaining of compatibility between the glaze and the biscuit from the temperature it started to harden, above 500 ºC, down to the normal temperature, with its highs and lows, at which the azulejos were supposed to be functional for centuries. Compatibility meant that the glaze had to be well connected with the biscuit so that it would not spall off but also that its retraction during cooling followed that of the biscuit to exclude the possibility of shivering and at room temperature was under slight compression to avoid visible crazing. The composition of the raw materials of the biscuits, the composition of the glazes that had to be compatible with them, and the second firing cycle that resulted in the final product were the most challenging problems to be dealt with.

2 THE CLAYS

Every potter aims at finding proper clay, meaning a raw material fit for the purpose of manufacturing glazed tiles. We know today that the best results could only be obtained with marl or else a mixture of clay with limestone. Piccolpasso (in his First Book) mentions the utilization of two sorts of raw material: one to which he calls *genga*, rich in calcium, fit for the production of majolica and cream in colour after firing; the other, poor in carbonates, fired red and was fit for kitchen ware. The calcium content resulted in the right thermal expansibility resulting, upon cooling, in a slight compression of the glaze that excluded crazing [op. cit: 27-28].

Sources converge in that for many centuries potters were not aware that a proper raw material could be obtained by mixing clay with milled limestone and so they depended on the finding of a deposit of suitable marl. Of course its suitability could only be established empirically by tentatively firing glazed tiles made from it. Kate van Lookeren-Campagne researched Dutch sources and showed that, once adequate marls had been found, potters knew they might be improved by mixing with other materials (such as sand or specific clays) but potters relied always on the same deposits, including imports from abroad and that notwithstanding the technological evolution, in Holland the situation was still the same at the end of the 18th century [8]. Bastenaire-Daudenart writes at a time when it is already possible to establish scientifically the desirable composition of the raw materials [op. cit: 27-32], and yet he regrets that many would-be potters were ruined in attempting to find a proper marl because they were unaware of the then modern means of analysis [op. cit: 11-13].

The information available points thus to the possibility of geographical attribution of productions based on a chemical analysis of the biscuits. But documents from the archives of Real Fabrica do Rato in Lisbon, dating from the early 19th century, show that there were several locations where the clays and marls were extracted (at least 17 in Portugal). This means that by this time it was easier, at least for a major factory, to obtain a suitable raw material (presumably by altering the composition through mixings) and a geographical attribution based solely on the composition of the biscuits at this late time may be impossible.

3 THE MANUFACTURE OF THE TILES / AZULEJOS

The clay / marl was mixed with water and screened and then mixed with sand on a 2: 5 basis. The mixture aimed at reducing retraction upon cooling and the resulting paste was beaten and knead by feet [9, p. 26]. Portuguese azulejos from the 17th century have thick biscuits (averaging 15 mm) often depicting layering (e.g. in cream and reddish) and conspicuous inclusions, usually small stones, and hollows. Later productions show an increasing efficacy in the screening of the clays and homogeneity of the paste, corresponding to technological improvements.

In Portugal the first description of the technology for shaping tiles that we know is in a manual on construction materials written in 1882 [10]. The tiles were shaped by squashing the paste kneaded by hand into a mould in wood [9, pp. 28, 31]. After being moulded, the raw tiles were first piled and then laid on open shelves that allowed air to circulate over all faces and let to dry. While still malleable, the pieces were beaten to reduce the hollows and then brought to final shape by cutting them with the help of a metallic template [10, p 106].

Edges were broken with a pointed hammer to increase the area of adhesion to the mortar. The resulting irregular edges are called in Portuguese “escacilhado” and could be done, either before, or after the glaze firing. In the latter case the glaze does not run over the new faces and the area for adhesion is maximized. The actual solution used in a given case may help discriminate the workshop producing the tiles.

After the shaping, drying and, eventually, breaking of the edges, the ceramic tiles were fired for the first time.

4 THE KILNS

Piccolpasso describes and illustrates in great detail a majolica kiln used in Italy in the 16th century [op. cit. Libro II, sections 92-100]. Figure 1 reproduces one of the original plates depicting a rectangular kiln. In 1828 Bastenaire-Daudenart describes similar kilns ca. 2.70m wide by up to 4.00m deep adding that these were the only types used 30 or 40 years before but they had a number of shortcomings, including the fact that the wood was fed only along the axe and the temperature in the interior had considerable gradients. He stated that elyptic kilns, or at least with rounded corners were by then replacing the old rectangular types [op. cit: 103-122).

Lepierre, in 1899, ilustrates a rectangular kiln with rounded edges used by a Portuguese factory in Aveiro (figure 2). It had two superimposed chambers: on the top was fired the biscuit and on the lower one the glaze [op.cit. folding plate].

Figure 1: 16th century kiln as illustrated by Piccolpasso in Li Tre Libri dell'Arte del Vasaio

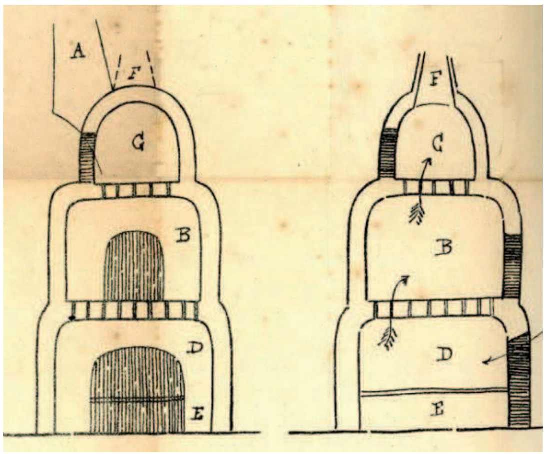

Figure 2: Kiln used by the Fonte Nova Factory in Aveiro in the late 19th century and ilustrated by Lepierre (op.cit.). The biscuit is fired in "C" and the glaze in "B". "D" is the fire chamber and "F" an exhaust

5 GLAZE AND GLAZING

Piccolpasso describes the manufacture of the raw glaze in two steps of which the first is the preparation of the *marzacotto*, a mixture of fine sand with plant ash (which was the source of potassium oxide) on a proportion of 3 to 1 in weight that was subsequently calcined and milled. The second step was the preparation of the *calcina*, a mixture of tin and lead, eventually with some sand added. The frit (raw glaze) was obtained mixing the *marzacotto* and the *calcina* and subsequently wet-milling the mixture [Piccolpasso, op. cit. Libri II & III, sections 62-64; 72-76; 182-183].

At the RFR in Lisbon, the lead and the tin were always acquired from British sources.

To apply the glaze, the frit was mixed with water and stirred until a milky suspension was obtained. The glaze was applied over the biscuit by letting it run over the surface, by dipping or with a brush. The density of the glaze was controlled through the volume of water added to prepare the suspension.

After the glaze dried the surface was hard enough to sustain contact and could eventually be transported to the shop of a painter and back to the potter's workshop. After the second firing a flawless white background was expected but rarely obtained. Almost all tiles present imperfections that may be very small (pit holes) or deface an important area (fissures or glaze crawling). In the 18th century, rather than repainting whole tiles and risk noticeable variations in hues of blue, the larger defects could be corrected with new glaze and if the glaze had already been fired, the tile was re-fired (figure 3). Such observations exemplify the historical value of tiles where defects of several sorts are apparent, from which valuable information can be gathered on the workshop practices.

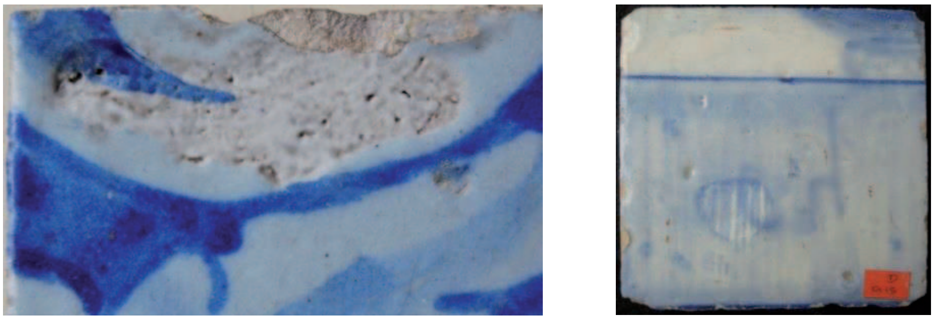

Figure 3: Retouchings with new glaze to reintegrate lacunae caused by defects in 18th century tiles (Museu Nacional do Azulejo items refª. A 159 and refª. A15 D)

6 PIGMENTS AND DECORATION

Painting over the raw glaze was described by Piccolpasso at a time when majolica was an art medium. The information he gives is applicable to Portuguese azulejos as well, up to the first half of the 19th century, when stencils were introduced to hasten the production of repetitive patterns.

The decoration was painted over the raw glaze. Colours could be different after firing. Cobalt blue could be obtained as a grey oxide (zaffre) however it could also be processed as blue smalt and it is likely that it was used mostly under this form [11].

In figurative panels the intensity of the blue could be varied by the addition of water. Because the raw glaze is made up of aggregated powder, when the paint is applied the water is absorbed and the pigment deposited. Each brush pass is clearly seen only after firing and each superposition, whether wanted or not, making any complex hand painting on faience a particularly difficult art, requiring great craftsmanship.

A recent publication made an overview of the use of cobalt blue in Portuguese azulejos and showed that the pigment used in Portugal since the 16th up to the second half of the 18th century had its origin in Saxonia and Bohemia. The same paper reviewed the technology used to obtain the pigment from the cobalt-bearing ore to zaffre and smalt [11].

Of all the pigments used, copper green, iron brown and manganese dark purple were likely produced locally given the accessibility of their raw materials. Manganese can be obtained from several different ores and is thus specially promising as a basis for sourcing the pigments. Blue smalt may also have been produced locally from cheaper imported zaffre.

7 TECHNO-HISTORICAL INFORMATION FROM SEM OBSERVATIONS

There are contemporary written sources, as mentioned, but many details remain unknown, either because they were considered a shop secret or, more often, because they were not considered relevant. To enlighten such aspects we have however a source available: the manufactured products themselves.

7.1 A PORTUGUESE 17TH CENTURY AZULEJO

Figure 4 is a backscattered scanning electron microscope (SEM-BSE) image of a section of a 17th century azulejo of Portuguese manufacture, painted in blue. The glaze and biscuit areas are indicated. The glaze is depicted with a lighter colour because of its high content in lead, an element with high atomic weight.

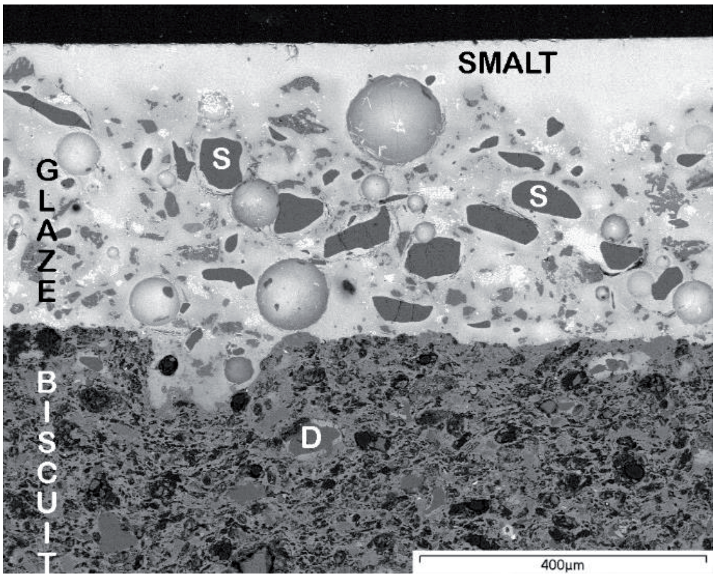

Figure 4: SEM-BSE image of a section of the glaze and biscuit of a 17th century Portuguese azulejo painted in blue. "S" are grains of sand (image acquired at the laboratory of the CSIC, Madrid, Spain)

Many grains of sand are to be seen in the glaze (two are indicated by the letter "S"). Their boundaries are very sharp and small fissures may be seen around the larger grains. These were formed when the glaze cooled under 573 ºC, the quartz underwent its beta to alfa inversion and the grains of sand contracted in a manner that the surrounding glaze could not compensate.

There is a layer on top, of a colour lighter than the rest of the glaze, where no grains of sand or other impurities are seen. That is a layer of blue smalt and the lighter colour indicates that it is richer in lead than the glaze and consequently lower-fusing. The smalt does not have tin oxide (small white crystals seen elsewhere in the glaze) and the fact that it does not have any inclusions whatsoever indicates that a fine milling was possible and consequently the presence of inclusions in the glaze does not derive from a technological shortcoming but is purposeful, probably to help render it opaque with less use of expensive tin.

There are several other details of interest, one of which has to do with the grains of sand in the biscuit. One of the grains is marked "D" and it is seen to be encircled by a substance slightly lighter in colour that fills a void that once existed around the grain, probably caused by the quartz inversion. An examination of the biscuit will reveal other instances of a substance of the same colour filling former voids. That substance is calcium oxide deposited by limewater that circulated through the porous biscuit. It indicates that the tile was applied on a moist wall and in time the calcium oxide will carbonate and form calcium carbonate.

7.2 A FLEMISH 16TH CENTURY AZULEJO

Figure 5 is the image of a similar section taken now in a Flemish tile manufactured in Antwerp in 1558 [12]. This part of the tile is painted in yellow and the lead-rich pigment does not dissolve in the glaze and may be seen as a layer of white fragments marked "Y". In Portuguese azulejos this colour layer is always at the surface because it does not sink into the glaze but here it is covered by a layer without small crystals of tin oxide, grains of sand or any other inclusions. This is a layer of clear glass called "coperta" originally used as a protective upper layer by Italian majolica manufacturers and to which Piccolpasso refers, recommending that it should be sprinkled with a brush to avoid disturbing the painting already applied. Indeed it is easily recognized that since the yellow layer seems to wave, even touching the surface, the *coperta* must have been sprinkled over the finished paint.

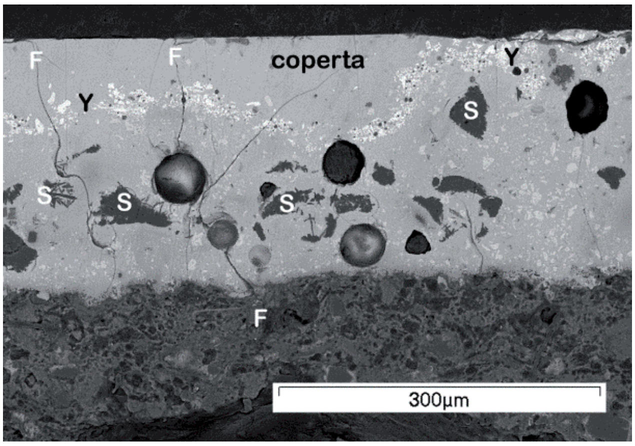

Figure 5: SEM-BSE image of a section of a 16th century Flemish azulejo painted in yellow (pigment "Y"). "F" marks fissures in the glaze. "S" are grains of sand transforming into a high temperature form of silica (image: LNEC)

A number of grains of sand are seen inside the glaze, some of them marked "S". However, their boundary is not sharply defined, as in the Portuguese azulejo, and the smaller grains are seen to have transformed into separate flat-shaped crystals. This is because the glaze was fired at a high temperature and probably kept at the top temperature for a relatively long time and the grains of sand transformed into a high-temperature polymorph of silica (tridymite or cristobalite), a change that is not reverted when the glaze cools.

The fissures around the grains of sand, that were so apparent in the section shown in figure 4, are absent here, even in the case of relatively large grains of sand that were cooled when they were just starting to re-crystalize. This observation suggests that, either the cooling was slower, or else the glaze was softer than that in the Portuguese azulejo when the cooling attained the quartz inversion, allowing for a re-arrangement.

However a number of fissures are seen in the glaze (some of which marked "F"). One of those can be seen to enter the biscuit and propagate into it. This suggests that during the lifetime of the tile, it was kept for a relatively long time in a moist environment - the biscuit expanded up to a point when the glaze, that does not absorb moisture, crazed because it could not meet the expansion.

Figure 6 shows a SEM-BSE image of a detail of the same section where a number of rhombohedral crystals are seen (some of which marked "C" in the image), often depicting a lighter core. These crystals are rich in silicon and started nucleating around a tin oxide crystal formed at a higher temperature. The fact that the main component of the glaze is crystallizing instead of forming the amorphous glass structure means that the cooling must indeed have been very slow and consequently some devitrification occurred. This devitrification happened during the firing of the glaze and should not be confused with a form of decay.

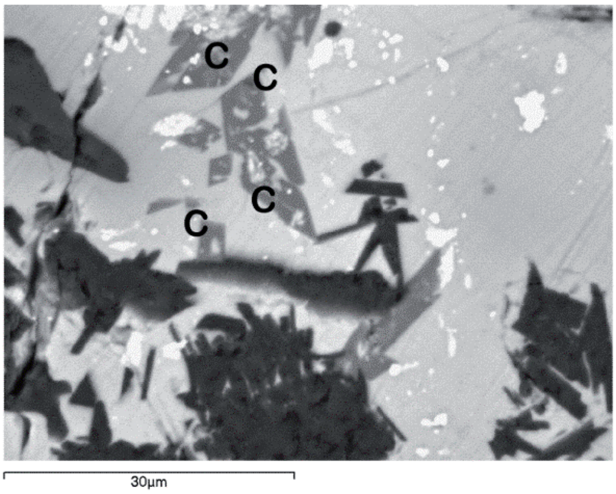

Figure 6 : SEM-BSE image of a section of a 16th century Flemish azulejo depicting devitrification crystals "C"

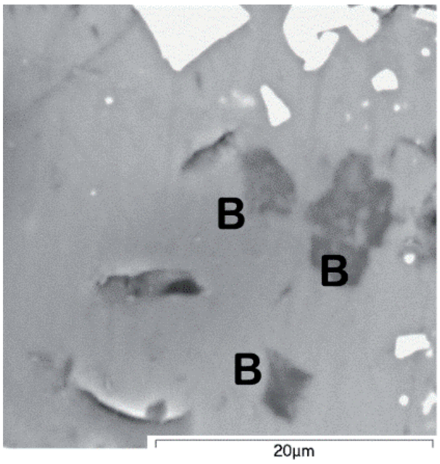

Figure 7 : Another detail of the same section with inclusions "B" rich in P and Ca (both images taken at LNEC)

On figure 7 a number of peculiar rather indistinct crystals can be seen and were singled with the letter "B". These were never seen in Portuguese azulejos and are of a compound rich in phosphorus (P) and calcium (Ca) and probably mean that at this particular workshop bone dust was added to the glaze frit, possibly for added opacification. The resulting content in P (ca. 3%) can be capital for the attestation of a provenance.

7.3 A PORTUGUESE 20TH CENTURY AZULEJO BY JORGE COLAÇO FOR FABRICA LUSITÂNIA

Figure 8 shows part of a panel painted in 1932 by Jorge Colaço on *Fábrica Lusitânia* to line the façade of the Church of St. Ildefonso in Porto. At this time he was painting in the glaze - previously he had painted over the glaze [13] - and yet his work depicts an extraordinary control over the difficult cobalt blue pigment. A small scale that had spalled from the façade was retrieved and Figure 9 shows two SEM-BSE images thereof. On the left side image can be seen that, extraordinarily, the glaze is made up of two layers: a basal layer ("1") which must have been fired with the biscuit since there is no clear borderline in the interface, as seen e.g. in the examples of figures 4 or 5. Over this stands a second glaze layer ("2") whose lighter colour points to a higher content in lead. The picture on the right side of figure 9 depicts a small boundary area between the two layers and it is evident that they did not fuse together and the opacifier used (an arsenic compound) did pack on the interface and inside the gas bubble but seemingly could not cross the border. An analytical procedure by energy-dispersive X-ray spectroscopy (EDX) associated to the SEM revealed that the proportion between the contents in Si and Pb is ca. 1.5 in the lower layer, but only 0.7 in the upper layer. This means that layer 1 has the composition of the glazes normally used in Portuguese azulejos, but the upper layer is much richer in lead than usual and consequently can be fired at a much lower temperature.

Figure 8: Panel painted by Jorge Colaço in 1932 for the façade of Igreja de Santo Ildefonso, in Porto, Portugal (image from Wikimedia Commons)

A complete picture of the consequences of this technology can only be achieved through reproductions; however it is entirely plausible that the lower layer only serves to ensure a good connection between the glaze and the biscuit, while the upper layer easily connects to its lower counterpart because they are of the same “nature”. Being low-fusing permits the second firing at a low temperature, avoiding too much spread of the blue pigment and granting the painter the possibility to impart a watercolour-like quality to his art work.

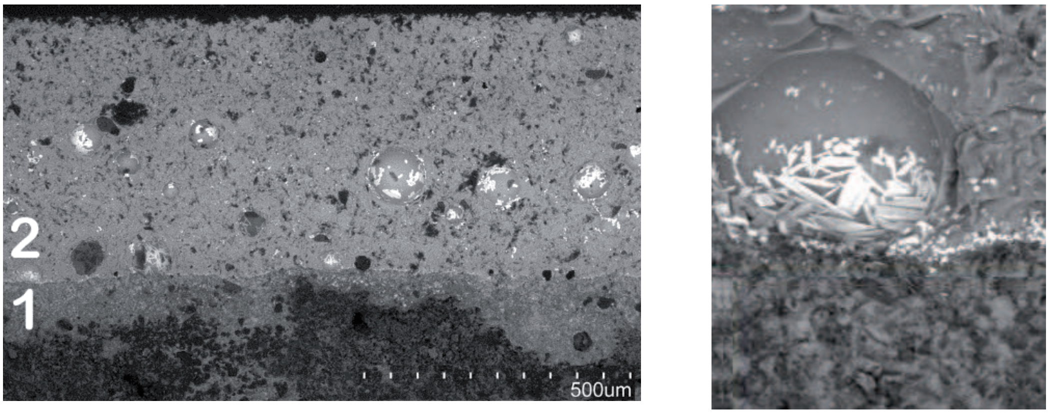

Figure 9: Left: section of a circa 1930 Portuguese azulejo painted by Jorge Colaço on Fábrica Lusitânia depicting two glaze layers “1” and “2”; Right: detail of the same section showing the interface between layers (HERCULES Laboratory)

8 CONCLUDING NOTES ON THE CONSERVATION AND RETRIEVAL OF THE TECHNO-HISTORICAL VALUE

A recent publication has shown that azulejos could be restored by re-firing and that when properly used the method permitted recovering the whiteness of the faience, eliminate crazing and generally improve the aspect to an apparent newness (figure 10) which was maybe the only shortcoming of the technique [14]. Another publication pointed that the mere idea of restoring glazed ceramics through the arts of fire brought forth methodologic arguments unparalleled in other restoration methods, and discussed the re-firing of azulejos based on theoretical restoration principles [15].

Cases such as those illustrated in figure 3 show that re-firing in itself is not macroscopically damaging even in the very long run but how does it affect the microscopic information?

Having asserted that azulejos, as most all other artefacts, have a specific techno-historical value derived from information they contained on the technology that produced them, we now consider how this value will be diminished by re-firing at the conditions specified (a maximum temperature of 890 ºC for 45 minutes) [14, 15]. The notes offered here are based on the experiments done so far and the extent of our knowledge at present, namely about the temperatures originally attained in the kilns and supposed to be in excess of 900 ºC for a relatively long period of time. The reasoning in this section must one day be verified through a lengthy series of experiments using reproductions manufactured under controlled conditions and successively re-fired at increasing temperatures.

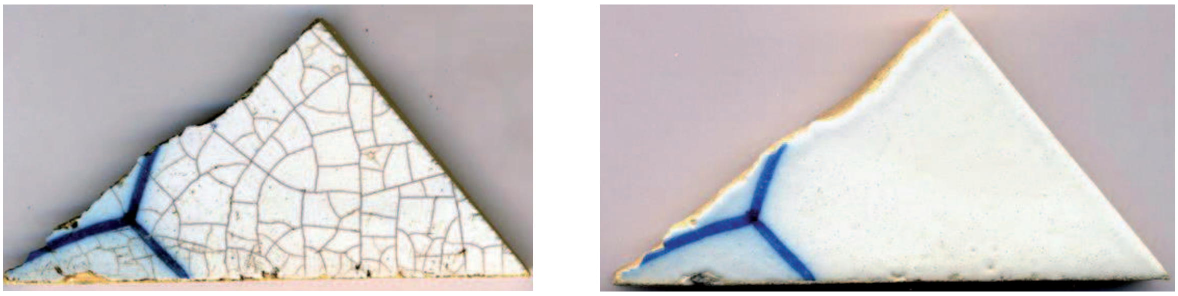

Figure 10: An azulejo fragment before and after restoration by re-firing (image: LNEC, from [15])

The re-firing of a tile does not introduce new elements in the composition, except, eventually for those available in the air. An azulejo such as illustrated in figure 4 and discussed in section 7.1 will likely not suffer any alteration in the composition of the glaze or, noticeably, in the mineralogical composition of the biscuit. The minute fissures of the glaze around the grains of sand seen in figure 4 may, or not, be conserved depending, not on temperature, but rather on the cooling rate. Any contaminations with organic material will be volatilized (hence the re-acquired whiteness) but those were not part of the techno-history of the tile. They were, however, part of the historicity related with the passing of time and whenever the item shows a patina, the patina will be lost [15]. The re-firing of the tile illustrated in figure 5 and discussed in section 7.2 would, besides, cause the fissures that cross the glaze to close. If they were wide, there would be an internal re-arrangement with morphological distortions and the gas bubbles once crossed by fissures would be rendered elliptical in shape.

The re-firing of a tile such as that illustrated in figure 9 and discussed in section 7.3 at 890 ºC for 45 minutes, however, would cause both glaze layers to fuse and likely coalesce, possibly resulting in an indistinct boundary between them. Not only the techno-value would be substantially affected in its most interesting aspects, but also, if the tile was painted, the pigments would likely be displaced and the artistic value of the image, which conservation aims to preserve above all, would at least be altered and possibly even ruined. This last example was chosen to stress that, in this case as in most all others, techniques cannot be applied blindly as each case may have specificities that must be understood before irreversible actions are taken.

The techno-historical value is an important part of the historical value. In faience it is maintained in the fractions even when the object is fragmented. It is unapparent to most, but that fact does not decrease its importance. That value may be conserved, impaired, or lost following a restoration and, albeit keeping in mind the precedence of the artistic value, the techno-value is certainly worth to be understood, respected and, whenever possible, conserved. It calls for an insight on the technologies behind an artefact and working knowledge of how to obtain the information it preserves. As time goes by, more sophisticated instruments become available and the techno-value increases because more information can be extracted. In its increase with time it parallels the antiquity value but for a different reason and certainly at a much faster rate. Any tools available should be used to the fullest extent and a congregation of knowledges in several fields achieved within the research team is an essential step to accede to the wealth of hidden information which, once obtained, may lead to new finds or, at least, establish on sound scientific grounds the mere conjectures of today.

9 REFERENCES

1- Riegl, Aloïs "The Modern Cult of Monuments: its Essence and its Development" in Historical and Philosophical Issues in the Conservation of Cultural Heritage (Reading 6, pp. 2), Ed. N.Price, M.Kirby, J. Paul Getty Trust, Los Angeles, USA 1996.

2- Dumortier, Claire, "Céramique de la Renaissance à Anvers", Editions Racine, Brussels, 2002.

3- Pais, Alexandre; Mimoso, J.M; Dumortier, C, Esteves, M.L; Silva, M.A; Pereira, S.R.M, "Graça Church revisited" in Proc. Int. Conf. Glazed Ceramics in Architectural Heritage (GlazeArch2015), pps. 35-40. Lisbon, Laboratório Nacional de Engenharia Civil (LNEC), 02-03 July, 2015.

4- Piccolpasso, C., "The Three Books of the Potter's Art"(*Li Tre Libri dell'Arte del Vasaio* translated and edited by R. Lightbown and A. Caiger-Smith), London, 1980.

5- Lepierre, C., "Estudo Chímico e Technologico sobre a Ceramica Portugueza Moderna", Imprensa Nacional, Lisbon, 1899.

6- Bastenaire-Daudenart, F., "L'Art de Fabriquer la Faïence Recouverte d'un Émail Opaque Blanc et Coloré", Librairie De Malher, 1st edition, Paris, 1828.

7- National Archives Torre do Tombo, Books 384, 551 et al. partially transcribed in "Real Fabrica de Louça ao Rato", Museu Nacional do Azulejo / Museu Nacional de Soares dos Reis. Lisbon / Porto. 2003.

8- Lookeren-Campagne, K., "Een verkeerde loop in 't vuur: an initial investigation into what Dutch archival sources can tell us about techniques and problems in the production of 17th and 18th century Dutch tin-glaze tiles", in Proc. Int. Conf. Glazed Ceramics in Architectural Heritage (GlazeArch2015) pps. 27-33. Lisbon, LNEC, 02-03 July, 2015.

9- Ferreira da Silva, J., "Arte de Louceiro- Tratado sobre o modo de fazer as louças de barro mais grossas", Impressão Régia, Lisbon, 1804.

10- Rebello Pedrosa, A, "Materiais de Construção", Escola do Exército, 5ª Cadeira, 1ª Parte, Lisbon 1882.

11- Mimoso, J.M., "Origin, early history and technology of the blue pigment in azulejos", in Proc. Int. Conf. Glazed Ceramics in Architectural Heritage (GlazeArch2015) pps. 358-375. Lisbon, LNEC, 02-03 July, 2015.

12- Mimoso, J.M., Silva, A.S., Martins, I.M., Costa, D.R., Pereira, S.R.M., Esteves, L., Pais, A.N., "Analytical study of tiles of presumed Flemish origin from the Palace of the Dukes of Braganza in Vila Viçosa", in Catalogue of the exhibition "O Testamento de D. Teodósio" pps 62-72, Museu Nacional do Azulejo, Lisbon, 2012.

13- Santos, C. E., Vieira, E., Mirão, J., Mimoso, J.M., "Jorge Colaço um artista multifacetado. Estudo e caracterização das técnicas de pintura em azulejo" in Proc. Int. Conf. Glazed Ceramics in Architectural Heritage (GlazeArch2015) pps. 91-109. Lisbon, LNEC, 02-03 July, 2015.

14- Chaban, A., Pereira, S.R.M., Esteves, L., Peddis, F., Mimoso, J.M., "Restauration of semi-industrial glazed ceramic tiles by re-firing" in Proc. of the Int. Conf. Glazed Ceramics in Architectural Heritage (GlazeArch2015) pps. 185-195, LNEC, Lisbon, 02-03 July, 2015.

15- Mimoso, J.M., Chaban, A., "A theoretical approach to the restoration of azulejos by re-firing" (in Portuguese with English abstract) in *Conservar Património 23*, pps. 55-61, doi:10.14568/cp2015044, 2016.

Acknowledgements

Our thanks to the HERCULES Laboratory of the University of Evora in Portugal, to the CSIC in Madrid and to our colleagues Alexandre Nobre Pais and Antonio dos Santos Silva for samples and for generously contributing their time and access to instrumental means. A thought to all our co-authors in the papers listed in the reference section. Memorable results derive from a gathering of knowledges in a friendly environment.

Thanks to Eduarda Vieira for that revealing minute sample collected on the pavement in Porto.

Research by Maria de Lurdes Esteves under an IIFA / University of Evora PhD project funded by the Portuguese Foundation for Science and Technology (FCT) under protocol IMC-PROP/5170/2011.

Research by João Manuel Mimoso integrated in Project FCT-AzuRe - Estudos no Azulejo Português para Candidatura a Património da Humanidade funded by Fundação para a Ciência e a Tecnologia under contract PTDC/EPH-PAT/5096/2014.