GlazeArt2024

International Conference
Glazed Ceramics in Cultural Heritage

Editors
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Edited by João Manuel Mimoso, Dória Costa,
Sílvia Pereira and Marluci Menezes

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Preface

Glazed ceramics and particularly faience (majolica, if you prefer) are an artist's dream and an engineer's nightmare. A dream because, when painted, the decoration becomes sealed in glass and potentially forever lasting and shiny; a nightmare because they go against the most basic recommendations an engineer would put forward about a material. Laminated materials are problematic because their properties change abruptly, which is always a source of concern for the engineer. But glazed ceramics such as azulejos take that proposition to extremes by lining a very porous ceramic material that expands when moist, with impermeable glass that does not expand at all and totally cuts the vapour transmission from the ceramic biscuit to the environment, with only a micrometric interface between them. These problems are compounded by architectural integration and therefore glazed ceramics such as azulejos represent a summit of technological achievement by trial-and-error that does not cease to amaze those who dwell into the technical intricacies involved. The majolica technology of rendering a transparent glaze opaque and containing the spread of pigments in a way that allows fine painting over it through a recrystallization of minute tin oxide crystals is another technical triumph which someone singled as the first nano technology developed by man.

There are also plenty of reasons of appeal to historians, given their extraordinary antiquity, the evolution and spread of know-how for over 3,000 years, the establishment of specialized workshops with the master-apprentice micro societies under medieval and renaissance guilds, the flow of raw materials and processed pigments and the final establishment of semi-industrial production. And there certainly is no need to point the sheer beauty of Italian maiolica, Islamic tile linings or Portuguese azulejos because it is well-known to aesthetes and a subject of the art-historians work.

Remains are also of great interest to archaeologists, because excavations often bring to light centuries-old shards in a remarkable condition that may help establish trade routes, determine the local technological advancement and possibly contribute to the fine-dating of other conjoined findings.

The duality of art content and its material embodiment calls for a co-operation between Art Historians, Materials Engineers, Chemists, Geologists and Instrumental Analysts and was the ground for the fruitful understanding established in Portugal since 2009 between a number of partners, namely the *Museu Nacional do Azulejo* (National Tile Museum), the Nova University of Lisbon, the HERCULES Laboratory in Évora, and *Laboratório Nacional de Engenharia Civil* (LNEC) that allowed substantial advances in the study of Portuguese azulejos and other heritage faience, shedding light on issues previously considered very hard to settle.

This Conference, organized under the European Project IPERION HS and the National FCT-funded Project CHROM-Az called for a decisive effort from the members of both the Organizing and the Scientific Committees and to all goes our thanks. LNEC staff is acknowledged for the local organization and support to the conference. Last, but indeed not least, our appreciation goes to all authors whose contributions are the body of the Conference. GlazeArt2024 follows the successful GlazeArt2018 and GlazeArch2015 conferences and affirms our common aim to organize a string of conferences to help expand the network of co-operations towards the understanding and preservation of not only azulejos or majolica, but the whole glazed ceramics heritage.

João - Manuel Mimoso

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Index

Unveiling the colours of Portuguese *Azulejos* between the 16th and the 18th centuries: The ChromAz project

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SUMMARY: This communication describes the project ChromAz – The Chromatic Journey of the Portuguese Azulejo, funded by the Fundação para a Ciência e a Tecnologia (PTDC/HAR-HIS/1899/2020).

KEY-WORDS: Azulejo; glaze; glazed tile; material characterisation; research project

The Portuguese azulejo (glazed tile) heritage is internationally recognised as unique, much due to its original and uninterrupted use in the most diverse architectural spaces since the 16th century. This heritage has been given increasing attention in the last decades; however, its production techniques are still being studied.

In 2021, the ChromAz project, funded by the Fundação para a Ciência e a Tecnologia (PTDC/HAR-HIS/1899/2020), began a 3-year study on the colours used in Portuguese azulejo since its beginning in the late 16th century until the mid-18th century.

The project was designed to investigate three main axes of azulejo heritage: colour palette [1], recipes, and chemical composition. This communication addresses the methodology and work completed so far.

The methodology combines historical research with the analytical characterisation of selected samples to identify the pigments that make up the Portuguese tile palette (Figure 1). The collection of the National Tile Museum, in Lisbon, was the starting point for wider research on the colours used during the period under study. Important in situ panels (e.g., the Academy of Sciences and the Calheta Palace, in Lisbon) are being studied as well. A multi-analytical methodology covering elemental, molecular and structural analysis, was developed to enable the identification of all glaze components.

Contrary to Italian maiolica or Dutch delftware, there are no known treatises or recipe books on Portuguese ceramics before the 19th century, making the historical tiles the sole testimonies of practical knowledge that has been lost over time. Therefore, the results obtained from the chemical analysis are the basis for the reproduction of the colours [2], along with the study of historical treatises and recipe books, such as the Italian treatise on maiolica by Cipriano Piccolpasso ("The Three Books of the Potter's Art", ca. 1557).

This project is a collaboration between several institutions: VICARTE (Glass and Ceramic for the Arts – FCT-NOVA), Universitat Politècnica de Catalunya (BarcelonaTech – Spain), Laboratory for Instrumentation, Biomedical Engineering and Radiation Physics (LIBPhys, FCT-NOVA - Portugal), the University of Antwerp (Belgium), the ARTIS - Institute of Art History (FLUL - Portugal), and the National Tile Museum (Lisbon, Portugal).

Figure 1. µ-EDXRF analysis of a 17th-century azulejo from Museu Nacional do Azulejo (Lisbon)

Figure 2. Laboratory replication of a Naples Yellow historical pigment recipe

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An assessment study of Islamic period tiles (Timurid, Ottoman, Safavid and Qajar) from 12th to 19th centuries to trace the glaze technology

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SUMMARY: In this study three instrumental techniques were applied to reveal the technological characteristics of the glazes and pigments of Islamic tiles (Timurid, Ottoman, Safavid and Qajar) from the 12th to the 19th centuries.

KEY-WORDS: Raman spectroscopy; pXRF; Islamic period; glaze; pigments.

Raw materials determine the final composition and properties of a fired ceramic. Distinctive minor (Ca, K, Al, Mg, etc.) and trace elements (Bi, Rb, Sr, Zr, etc.) of the geological context, which give significant signal, permit distinguishing the provenance and the phases characteristic of the firing procedures, thus differentiating different productions of tiles. In many cases, the most sophisticated part of the process is the formulation and fabrication of the glaze, especially the colored areas. Complete tiles, which are coming from identified historic buildings and exhibited in the museum showrooms are better documented concerning their origins rather than the unregistered fragmentary sherds. Therefore, a detailed analytical examination is required for these undefined tiles to identify where they are produced. Systematic studies with spectroscopic methods will lead to a statistical work in addition to the material culture and art historical research in the Islamic period (focused on the 12th and 19th centuries) ceramic art.

In this study, three techniques, Raman, portable X-ray fluorescence (pXRF) and scanning electron microscopy-energy dispersive (SEM-EDS) spectrometry were applied to reveal the technological characteristics of the glazes and pigments. Raman analysis which characterizes micro- and nano-structures of colored and transparent glazes, opacified or not, was applied to sherds mostly collected before the 1960s, preserved currently at the Louvre Museum [1]. These tiles were originated in Anatolia, the Caucasus, Iran, and Central Asia, which are, for most of them, characterized by the application of black lines to separate coloured areas. Similar fragmented sherds which are preserved in the reserves of Topkapi Palace Museum in Istanbul were also analysed with Raman spectroscopy if either they were produced in the Ottoman territory or if outside [2, 3]. Chemical analysis of glazes and colored areas were performed with pXRF for the sherds of the Louvre Museum (29 samples) and SEM-EDS for the Topkapi Palace fragments (4 samples). Figure 1 shows the similar sherds from Louvre Museum and Topkapi Palace Museum analysed for comparison. The reliability of pXRF measurements was formerly revealed when compared with the results carried out with SEM-EDS [4].

Figure 1. Representative tile sherds produced between 12th and 19th centuries from Louvre Museum (Paris, a-d, i) and Topkapi Palace Museum (Istanbul, e-h) collections.

Raman measurements of the collection of Musée du Louvre were carried out in the laboratory with a blue laser excitation and/or on the conservation site with a mobile device equipped with green laser[1]. The samples from Topkapi Palace Museum were analysed only with green laser in the laboratory [2, 3]. Comparison with XRF, SEM-EDS and IB composition measurement is made [5]. Three types of glazes were identified (Fig.2a): (i) a lead-rich glaze analogous to that of Byzantine, Zirid to Hafsid and al-Andalus productions, (ii) a lead-alkali glaze typical of the Ottoman productions of Iznik-Kütahya, and (iii) a mixed (poor lead/lead-free)-alkali glaze typical of Safavid productions.

Further comparison is made with the data collected with a different mobile XRF instrument on Edirne Mosque tiles [6] (Edirne was the first Ottoman capital) and with those recorded on sherds excavated from Ottoman Iznik kilns [7] (Fig.2b).

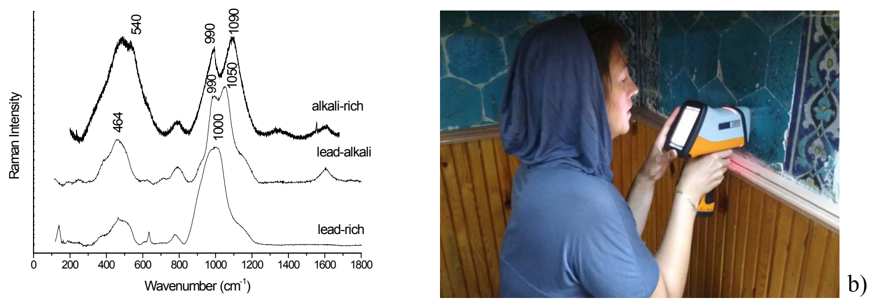

Figure 2. (a) Base-line substracted representative Raman spectra showing different types of glazes (lead-rich, lead-alkali, and alkali-rich). The baseline has been substracted in order to compare the bending to stretching band area ratio. (b) On-site measurement with pXRF in Edirne Şah Melek Paşa Mosque.

The colour depends on the precise composition of the glaze. The identification is not only based on the signature of the stretching mode of the SiO_4 tetrahedron (position of the wavenumber of the component(s)) but also on the position and shape of the continuous luminescence of the Raman background, characteristic of the raw materials used. For the determination of the luminescence, a wider spectral window up to 4000 cm^{-1} must be recorded with Raman, while the glaze signature only covers a spectral range between 300 and 1200 cm^{-1}. Lead-tin yellow, Fe-rich, Mn-rich and Cr-rich black pigments and opacifiers made of cassiterite and wollastonite were also identified in the colored areas. The Raman results (type of glaze and deduced processing temperature) were discussed in the light of the binary and ternary scattering plots showing oxide composition determined in the previous works (Fig. 3) and the microstructure examination on the polished section (defining single or multistep firing cycles).

Continuity was highlighted on the one hand between the tiles of Bursa, Edirne, and Istanbul (Ottoman Iznik-like production) and on the other hand between those of Samarkand area (Timurid) and Iran. Finally, the criteria determined from the study were applied to object from the art-market to identify artefacts.

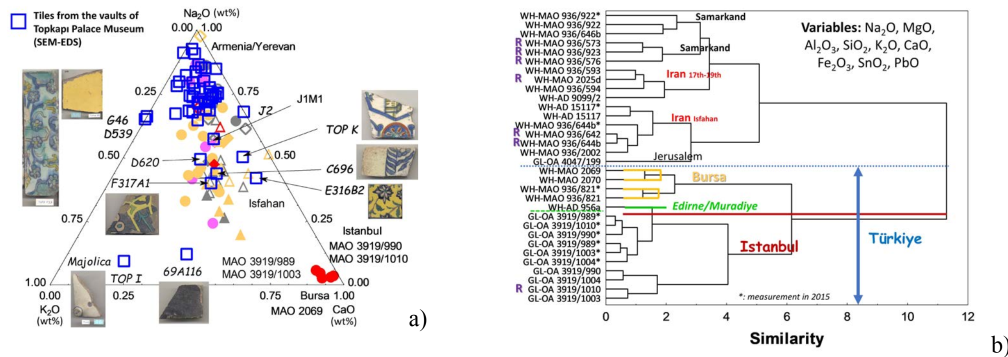

Figure 3. (a) Ternary scattering plot of fluxes (Na_2O, K_2O, CaO) and (b) hierarchical similarity dendrogram built from the variables (wt%) found in the white and transparent glazes.

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Tin-opacified glazes used in Italian maiolica: a compositional and lead isotopic study

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SUMMARY: A group of 30 shards of maiolica made in Montelupo Fiorentino between the end of the 14th and the 18th centuries previously analysed was compared with a group of 10 shards of maiolica made in Pisa between the 13th and 14th centuries. The compositional investigation of the samples was carried out by Scanning Electron Microscopy (SEM-EDS), while the lead isotope analysis was performed with mass spectrometry techniques (TIMS and ICP-MS).

KEY-WORDS: Archaeometry, Lead isotopes, Italian maiolica, Tin glazes.

Italian maiolica is one of the most representative vestiges of Medieval and Renaissance art, society and economy. Maiolica is an Italian term used to indicate tin-glazed earthenware. Tin-glaze technique originates in the Islamic world and arrived in Italy around the 13th century through the Iberian Peninsula. It is known that commercial trade between the Iberian Peninsula and the Republic of Pisa played a fundamental role in the diffusion of this technique in Italy and, in particular, in the Tuscany region [1], allowing the development of large production centres such as Pisa itself in the 13th century and, subsequently, Montelupo Fiorentino in the 14th century.
The aim of this research project, which is in its initial phase, is to broaden the knowledge of Italian maiolica production techniques and their evolution over the centuries through the comparison between different production centres. Namely, the productions of Andalusian Spain, Pisa and Montelupo Fiorentino, which were active for a long period of time between the 10th and 18th centuries, were selected. Another objective of the project is to investigate the origin of lead, an important raw material used as a flux to produce maiolica glazes [2]. Indeed, very little is known about the provenance of the raw materials used to produce these glazes. Lead is a common metal and is available locally in both Tuscany and Andalusia; however, previous studies on glazes highlighted the existence of long-distance trade routes for this raw material [3, 4].
The compositional investigation of the samples is carried out by Scanning Electron Microscopy (SEM-EDS), while the lead isotope analysis is performed with mass spectrometry techniques (TIMS and ICP-MS).

A first group consisting of 30 shards of maiolica made in the site of Montelupo Fiorentino between the end of the 14th and the 18th centuries (Fig.1) has already been investigated using SEM-EDS analysis. The results obtained about stratigraphy and chemical compositions of these samples are in agreement with those of late Medieval, Renaissance and late Renaissance maiolica reported by Tite in his review of Italian maiolica [5] (Fig.2). Another small group of 10 shards of maiolica made in Pisa between the 13th and 14th centuries (Fig.1) was analysed using SEM-EDS and compared with those of Montelupo Fiorentino.

Figure 1. The 30 samples of maiolica from Montelupo Fiorentino and the 10 samples from Pisa, listed by historical period of production.

Regarding the lead isotope analysis, 8 maiolica shards from Montelupo Fiorentino have been analysed to date. The isotopic composition highlighted that the samples are distributed into 2 distinct groups (called A and B) based on the historical period of production. This preliminary result indicates that lead isotopes could be a reliable tool for discriminating maiolica made in different periods. The comparison with the lead isotope composition of the deposits of the European and circum-Mediterranean area, from which lead was historically extracted, showed that the isotopic composition of the samples of Montelupo Fiorentino differs from that of the Italian deposits, suggesting that lead was imported from abroad (see Fig.3).

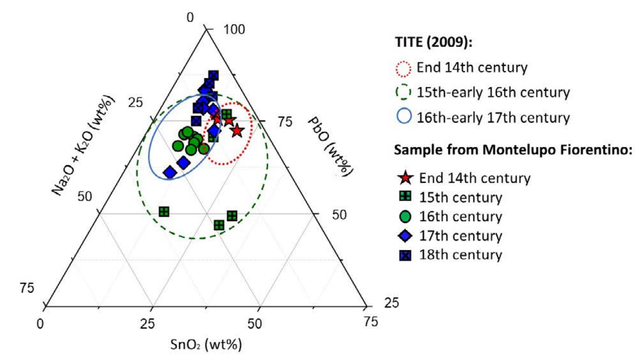

Figure 2. Chemical compositions of the Montelupo Fiorentino samples compared to those reported by Tite [5] regarding late Medieval, Renaissance and late Renaissance maiolica.

The samples are instead compatible with German lead ore deposits, in agreement with the proverb reported by Cipriano Piccolpasso [2] in his famous treatise about maiolica, written in c. 1557, 'piombo todesco, stagno fiandresco' ('German lead, Flanders tin'). At the same time, the lead deposits of Great Britain, Bulgaria, France and Switzerland are also isotopically compatible with the investigated maiolica glazes (see Fig.3). The information on the historical sources of lead extraction and trade towards Italy in the historical period investigated is scarce to the authors' knowledge, so that it was not possible to make further considerations.

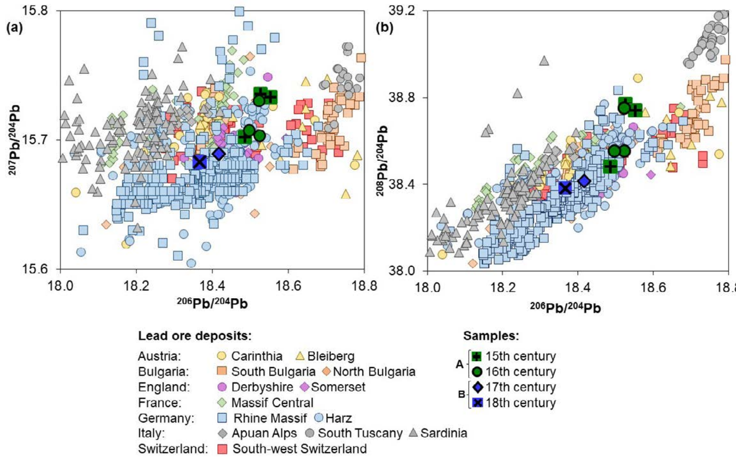

Figure 3. Lead isotope composition of the investigated samples compared with that of the main European lead ores. (a) $^{206}Pb/^{204}Pb$ vs. $^{207}Pb/^{204}Pb$; (b) $^{206}Pb/^{204}Pb$ vs. $^{208}Pb/^{204}Pb$.

This research represents an important opportunity to reconstruct the cultural and commercial exchanges, involving raw materials, artifacts and artisans in the Central European and circum-Mediterranean area, which promoted the birth and development of numerous centres of maiolica production in Italy. The prosecution of the project will allow us to compare both the technology and the origin of lead used in Montelupo Fiorentino, Pisa and Spain, thus acquiring information on the diffusion of tin glaze technology in Europe.

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'Steentjes' and 'Azulejos': a comparison of the tin-glaze of 17th and 18th century Dutch and Portuguese tiles

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SUMMARY: Tin-glazed tiles or "azulejos" were produced in Portugal from the middle of the 16th century and in the Netherlands from the beginning of the 17th century when they were termed steentjes meaning 'little stones'. In this paper, recent independent research into the chemical composition and morphology of 17th and 18th century Dutch tiles and Portuguese azulejos has been compared to determine what similarities and differences can tell us about their production process. Samples of historical tiles were analysed using scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM-EDX), the Portuguese azulejos having been analysed at the Laboratório Nacional de Engenharia Civil (LNEC) in Lisbon, and the Dutch tiles at the University of Amsterdam in the Netherlands. Cross-analysis of samples was undertaken to ensure that the results were comparable. The basic chemical composition of the Portuguese and Dutch glazes was found to be the same, comprising of silica, lead, tin and alkali fluxes with a PbO/SiO_2 ratio usually lower than 0.5 typical of tin opacified lead-alkali glaze. However, clear differences were observed in both the proportion of the elemental components and the glaze morphology. The Dutch glazes have been found to have a notably higher wt. % of Na_2O, MgO, CaO, SnO_2 and PbO, while the Portuguese glazes are higher in SiO_2 Al_2O_3 and K_2O. Regarding the morphology of the glazes, the Portuguese glazes consistently contain a high percentage of large unreacted inclusions and/or feldspar, a feature that is found to a far lesser degree in Dutch tiles in certain periods. The possible reasons for these differences are considered with relation to variations in the raw materials, notably the fluxes used, together with aspects of the firing process.

KEY WORDS: Tin glaze, azulejos, Dutch tin-glaze tiles, scanning electron microscopy.

Tin-glazed *azulejos* were produced in Portugal from the mid 16th century and in the Netherlands from the beginning of the 17th century. It is often assumed that the production techniques and recipes used to produce tin-glaze wares in Europe from the late 16th century will be similar as the technique was disseminated by Italian maiolica potters. Recent research comparing 17th and 18th century documents and studies of tin glaze production has indeed found that there was a surprising consistency in the materials and recipes used in the production of 17th and 18th century European tin glazes which broadly followed the low lead high alkali glaze descriptions in Cipriano Piccolpasso's *Li tre Libri dell' Arte del Vasaio* written in ca. 1558 [2]. In the case of Portuguese *azulejos* it has been observed that there was a shift of technology from high lead - low alkali to low lead - high alkali glazes from the 16th to the 17th century. While there are historical written sources on Dutch tin glaze production from the 17th and 18th century, such sources do not exist in Portugal.

The research discussed in this paper involves a comparative analysis of 17th and 18th century Dutch tiles and Portuguese azulejos glazes with the aim to gain greater insight into similarities and differences in the production process in the two countries. The analysis was undertaken using scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM-EDX). For the Dutch tiles, samples were taken from forty-five tiles from three different important production centra (Rotterdam, Harlingen and Utrecht) [1]. The Portuguese samples comprised of a selection of 21 reference azulejos mostly belonging to the collection of the Portuguese National Tile Museum (MNAz) which have been studied with the purpose to understand the evolution of Portuguese glazed tiles technology in Lisbon from the middle of 16th to the first quarter of the 19th century [2].

The clear differences in the chemical composition of the Portuguese and Dutch 17th and 18th century tin glazes can be observed in Figure 1. While the glazes contain the same basic composition, the Dutch glazes are seen to have a notably higher wt.% of Na_2O, MgO, CaO, SnO_2 and PbO, while with the Portuguese glazes the wt.% of SiO_2 Al_2O_3 and K_2O is higher. In general, the Dutch glazes have a higher proportion of flux. These difference in composition will be related to differences in the raw materials and/or the recipes used.

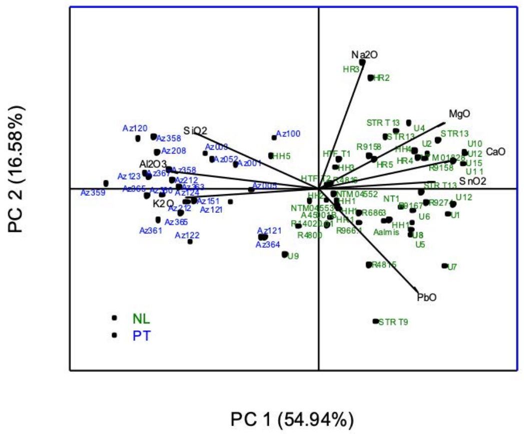

Figure 1. PCA of Portuguese and Dutch tile glaze 1600 – 1750

The high wt.% of Ca in the Dutch glazes could have several sources. Historic documents state that the sand used was from the Hague dunes which very likely contained calcium inclusions. Reconstructions of Dutch historic clay and glaze recipes showed a clear relation between the CaO wt.% of the ceramic and that in the fired glaze, unreacted calcium being observed to have migrated into the alkali-rich glaze matrix [1]. However, the fact that natural clays with a high $CaCO_3$ wt.% were also used in Portugal suggests that the observed differences in glaze composition and firing process (temperature or length of firing) must have significantly affected any diffusion of Ca into the glaze layer. Another source could be the potassium-rich plant ash used in the Netherlands which contained a high wt.% of Ca. The high Na wt.% could be due to the high proportion of sodium chloride (ca.12 wt.%) that is documented in historical recipes as being added at the final stage of glaze fritting.

The higher wt.% of K_2O in the Portuguese azulejos could be due to the use of potassium-rich plant ash as a flux. However, it is more likely to be related to the high proportion of coarse

inclusions in the glazes which include K-feldspar and are a feature of azulejos in comparison with the majority of Dutch glazes, as shown in the BSE images in figures 2 and 3.

The opacity of the Portuguese glazes is probably influenced by the large amount of crystalline inclusions while the Dutch glazes have a higher percentage of cassiterite (tin oxide) in a high-

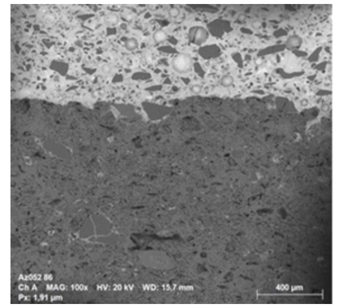

Figure 2. Azulejos, late 17th century [3]

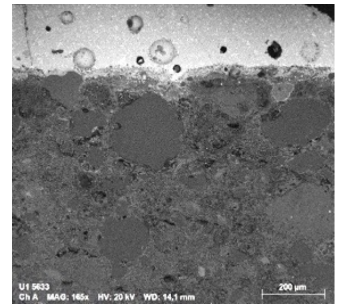

Figure 3. Dutch tile, late 17th century

flux glaze matrix. While some authors argue that such inclusions would not make a significant contribution to the opacity of the glaze because the refractive index of quartz would be comparable with that of the surrounding glaze [4], it is generally accepted that crystallites such as quartz and feldspar, together with gas bubbles, do act as opacifying agents and were used as far back as Medieval Mesopotamia [3].The increased amount of inclusions observed through the periods of Portuguese tin-glaze production can arguably be seen as an intentional (if not understood) means of opacification that reduced the need for a high proportion of expensive tin opacifier. The large quantity of inclusions may also suggest that a glaze mixture of a lead-tin calx and silica-alkali frit (possibly with additional sand) was applied directly onto the ceramic as mentioned by Piccolpasso, Dutch glazes having a second fritting stage.

The value of comparative research is clear and shown to provide new insights in Dutch and Portuguese tin-glaze production and further add to our understanding of European tin-glazes.

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Archaeometric studies of tiles produced in the Lisbon area (16th to 18th c.)

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SUMMARY: The information provided by the X-Ray Diffraction (XRD), X-Ray Fluorescence (XRF) and Stereo Microscopy (SM) techniques was used to characterize the ceramic bodies of the tiles produced in the Lisbon region, North and South of Tagus River, dated from the early 16th to the late 18th century. Despite of the enormous diversity of motifs, colours and number of tiles produced in the Lisbon region during that period, we could simply sort its ceramic pastes into four types.

For comparison purposes, a similar study was performed for cuerda seca and arista tiles belonging to museum collections or found in Lisbon archaeological contexts, and usually reported as Seville (Triana) productions (15th and 16th centuries) [1].

The biplots of the Potassium (K) versus Calcium (Ca) contents, normalized to the silicon content of each ceramic paste, for the Lisbon and Seville tiles, as well as the manganese content of each ceramic paste allowed us to exhibit manifest differences between the two production centres [1].

Confirming the traditional attributions, the compared results with those obtained on the Oratory of Garcia de Resende tiles (Évora) identified a Seville production.

KEY-WORDS: 16th to 18thc.; Lisbon tiles; Ceramic pastes; XRD, XRF.

Santo António da Charneca´s tile 16th c., 1st half

Acanto leaves's tile 17th c., 1st quarter

Corncob's tile 17th c., 4th quarter

Barroque tile, bat pattern, 18th c., 2nd quarter

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Analytic study of a renaissance azulejo panel depicting a coat of arms

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SUMMARY: The collections of the Museu Nacional do Azulejo in Lisbon include a 12-tile heraldic panel with a coat of arms set inside a cartouche in the Flemish style, crested with a Maltese cross. The drawing and painting are rather unskilled and the Maltese cross is particularly awkward, giving the notion that it was traced by hand directly over the glaze, maybe as an afterthought. The origin of the panel is unknown and it came to our attention because of the reddish colour of the biscuit, similar to the biscuits of the remarkable panel Nossa Senhora da Vida, exhibited nearby in the Museum, suggesting a 16th century production by the workshops of Lisbon. Two tiny samples were taken for study with a scanning electron microscope and energy dispersive spectrometer and the results confirm a production by a workshop within the technological circle of João de Góis, possibly around 1570.

KEY-WORDS: Renaissance azulejos; Flemish in 16th century Portugal; João de Góis; 16th century Lisbon azulejo workshops; Museu Nacional do Azulejo.

The collections of the *Museu Nacional do Azulejo* (National Tile Museum) in Lisbon include a 12-tile heraldic panel (Figure 1). The coat-of-arms depicts a contourné lion rampant on the dexter side and a hand holding a palm leaf on the sinister, and is set inside a cartouche in the Flemish style. The cartouche is surrounded by a green ribbon and crested with a Maltese cross. The whole is bordered in orange, simulating a wooden frame. The cartouche and frame are depicted as if illuminated from the left side of the viewer, but do not cast wholly coherent shadows on the background. The drawing and painting are rather unskilled and the Maltese cross is particularly awkward, giving the notion that it was traced by hand directly over the glaze, maybe as an afterthought.

Figure 1. The panel.

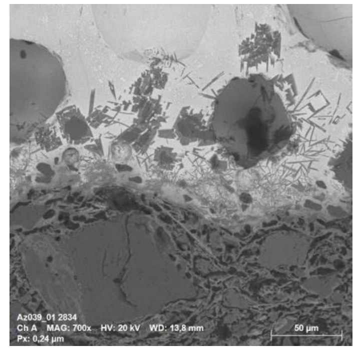

Figure 2. The interface.

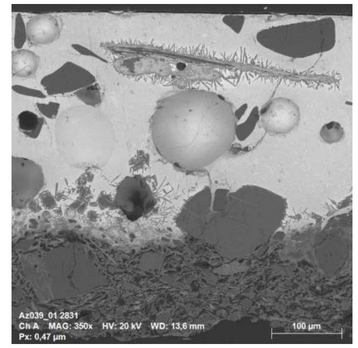

Figure 3. A "centipede".

The origin of the panel is unknown and it came to our attention because of the reddish colour of the biscuit, similar to the biscuits of the remarkable panel *Nossa Senhora da Vida*, exhibited nearby in the Museum, suggesting a 16th century production by the workshops of Lisbon. Two tiny samples were taken for study with a field-emission scanning electron microscope and an attached energy dispersive spectrometer (FE-SEM / EDS).

The glazes depict a morphology compatible with known works by the Lisbon workshop of João de Góis (name adopted locally by the Flemish potter Hans Goos), including the neo-formed interfacial K-feldspar crystals (Figure 2) and the occurrence of minute sheets of K-mica in the glaze that we call "centipedes" because of the crystalline outgrowths (Figure 3) [1, pp. 56-57]. The distinctive interface was experimentally duplicated through majolica reproductions made by our team, showing that it results from the lead-rich glaze composition and a particular firing schedule.

The composition of the glaze is characteristic of what we called "the circle of João de Góis" [2, p. 131], quite unique when compared to contemporary Spanish and Flemish productions because of its low contents in sodium and potassium and high in tin and in lead [3, p. 40]. Figure 4 compares an EDS compositional spectrum of the glaze of one of the samples with the same for a glaze of one of the tiles at *Igreja da Graça* that bear the monogram of João de Góis [1, p. 50]. As may be seen graphically, the compositions are close.

The composition of the biscuits is also characteristic of the clays from the region of Lisbon, with low contents in calcium and magnesium and relatively high in aluminium and potassium [2, p. 41]. Although not unique, their Ca/Si ratios of around 0.30, and sometimes less, are the lowest we know used at this time in majolica tiles made in Spain or in Flanders. Figure 5 compares an EDS compositional spectrum of the biscuit of one of the samples with the same for a sample taken from a sublayer of the *Forno do Tijolo* Miocene clay from the region of Lisbon which, although with a somewhat lower content in sodium (Na) and higher in iron (Fe), depicts the same characteristic highs and lows in the elements referred above.

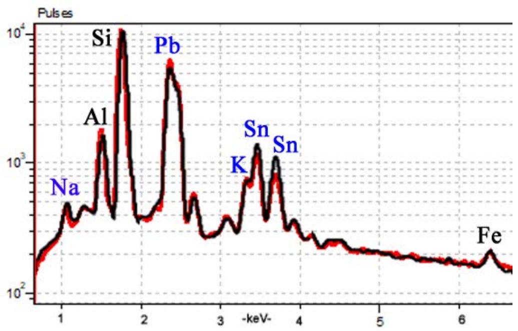

Figure 4. Compositional spectrum of the glaze of a sample from this panel (red) vs. spectrum of the glaze of sample L3 taken from a tile signed by João de Góis (black)

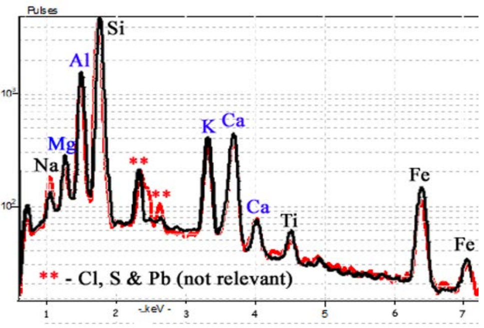

Figure 5. Compositional spectrum of a sample of biscuit from this panel (red) vs. of Lisbon clay sampled from the grounds of LNEC at a depth of 34.8 m (black).

The yellow pigment was analysed and seen to be of the lead-antimony-zinc type.

In conclusion, the panel was produced in the 16th century in Lisbon, with the distinctive technology of the circle of João de Góis. The glaze composition is particularly close to that of the glazes of the tiles at *Igreja da Graça* bearing the monogram of João de Góis and presumably datable to the second half of the 1560s, suggesting that the panel may have been manufactured around 1570. However, a firm chronology can only be established on historical grounds but the original location of the panel or its purpose remain undetermined.

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Remains of a mysterious floral panel painted in blue over a golden background

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SUMMARY: A visit to the Theological College of St. Paul in Almada, near Lisbon, revealed that several tiles of undetermined age and origin, displayed in two frames, were actually the remains of one or more panels with a floral design in blue over a yellow background similar to the well-known lining of Capela de São Roque in St. Roch's church in Lisbon, dated "1584". We present an analytic study of those tiles which may be attributed to the 16th century Lisbon workshop of the Flemish João de Góis or to another contemporary workshop within the same technological circle.

KEY-WORDS: Renaissance azulejos; Flemish in Portugal; João de Góis; 16th century Lisbon azulejo workshops; Capela de São Roque.

Two walls of *Capela de São Roque* in St. Roch's Church in Lisbon are lined with azulejo panels dated "1584" in which the figures are set against a scenery of blue floral designs over a background painted in yellow, presumably aiming to simulate the colour of gold [1]. For more than a hundred years that artistic solution, possibly inspired by Flemish panels once extant in Lisbon, has been considered unique in the country. However, a close observation of the walls of the same Church reveals two tiles once part of another panel in the same style. A third panel, found occluded in the Cathedral of Setúbal, was studied and published by our team in 2019 [2]. We were informed of the presence of two frames with old tiles in the Theological College of St. Paul in Almada, near Lisbon, and a visit revealed the remains of one or more similar panels (Figure 1) of unknown origin that may have been part of a now lost lining in a previous Convent founded in 1569 at the same site. After all, the panels in São Roque were not unique but seemingly represent the apogee of a local tradition in 16th century azulejo decoration, possibly with Flemish roots.

Figure 1. The two groups of azulejos conserved at the Theological College of St. Paul.

Most tiles in the group of seven from Almada have cream- or light orange-coloured biscuits but one, the only one marked on the back (A10), has a distinctly reddish biscuit, suggesting the possibility of two different clays and panels. However, the designs cast an orange shadow over the background, a unique trait common to all tiles, showing that they were likely once part of the same lining. Six tiny samples were taken for study by field-emission scanning-electron microscopy with associated energy-dispersive X-ray spectroscopy (FESEM-EDS).

The glazes depict a morphology compatible with known works by the Lisbon workshop of João de Góis, including the neo-formed interfacial K-feldspar crystals and the occurrence of minute sheets of K-mica in the glaze that we call "centipedes" because of the crystalline outgrowths (Figure 2) [3, pp. 56-57]. The distinctive interface was duplicated through majolica reproductions made by our team, showing that it results from the lead-rich glaze composition and a particular firing schedule.

The composition of the glaze is characteristic of what we called "the circle of João de Góis" [4, p. 131], quite unique when compared to Spanish and Flemish productions because of its low contents in sodium and potassium and high in tin and in lead [3, p. 40] with Si/Pb ratios of 0.35 ±0.5 in all samples.

The cream-coloured biscuits have a Ca/Si ratio above 0.50 and the clay, with a characteristically low Mg content, may have been taken from a specific Ca-rich sublayer of the Lisbon *Forno do Tijolo* Miocenic deposit. Else, it may derive from a mixture of clays. However, the red biscuit has a different composition with a Ca/Si ratio under 0.20, referable to a different, thicker, sub-layer of the same deposit. This would not be particularly noteworthy but for a detail: the yellow pigments are also different. The first tile was painted with a Sn-Sb-Pb yellow; the second with a Sb-Pb (Naples) yellow. The orange colour was obtained by mixing the yellow pigment with red iron particles.

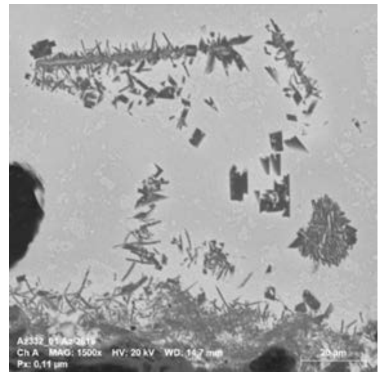

Figure 2. Interface and "centipede".

We conclude that the panel, or panels, were manufactured in Lisbon from the late 1560s to the 1580s by one or more workshops using the technology of the circle of João de Góis, while the occurrence of two clays and two pigments may indicate a production in two instances.

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A lost renaissance azulejo panel in the Cathedral of Setúbal

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SUMMARY: Works at the Cathedral of Setúbal revealed, behind a wooden decoration, the remains of what must have once been a remarkable renaissance azulejo panel at one side of the intrados of the arch of a chapel. The surviving tiles are decorated with foliage, flowers and fruits painted with a free hand. For mid tones the painter used a cross hatch technique unknown from other panels of the period. The lower part depicts what seems to be the base of a vase drawn with sharp dark lines and painted in blue with soft midtones.

We did an analytical study of samples taken from some of the tiles and concluded that they were manufactured in the 16th century by a workshop in Lisbon within the technological circle of the workshop of João de Góis.

KEY-WORDS: Renaissance azulejos; Flemish in Portugal; João de Góis; 16th century Lisbon azulejo workshops; Cathedral of Setubal.

In the 1940s the historian Vergílio Correia remarked on how few 16th century tile panels of Portuguese manufacture were known. Recent dedicated research has resulted in the identification and attribution of a substantial number of new cases, such as this we now report. Works at the Cathedral of Setúbal (reconstructed before 1570) revealed, behind a wooden decoration, the remains of what must have once been a remarkable renaissance azulejo panel at one side of the intrados of an arch (Figure 1). The surviving tiles adjacent to the edge are decorated with foliage, flowers and fruits painted with a free hand. For mid tones the painter used a crosshatch technique unknown from other panels of the period (Figure 1b). The lower part of the pier depicts what seems to be the base of a vase which, unlike the floral decoration, is drawn with sharp dark lines and painted with soft midtones (Figure 1 c). The remains are probably part of a 6-tile wide decorative festoon around the arch intrados. The tile dimensions (10 x 10 cm) are unusual, being the smallest known from this time, but were probably opted to cover the width of the area with six tiles, instead of with four 15 cm tiles.

Figure 1. a, b, c (left to right). Figurative elements on the left and lower sides of the remains.

A number of small samples were taken, of which three were prepared for analyses with field-emission scanning electron microscopy with associated energy-dispersive X-ray spectroscopy (FE-SEM / EDS). The glazes depict a recurrent morphology compatible with known works by the Lisbon workshop of João de Góis, including the neo-formed interfacial K-feldspar crystals and the occurrence of minute sheets of K-mica in the glaze that we call "centipedes" because of the crystalline outgrowths (Figure 2) [1, pp. 56-57]. The distinctive interface was reproduced by our team through replication attempts, showing that it results from the lead-rich glaze composition together with a particular firing schedule.

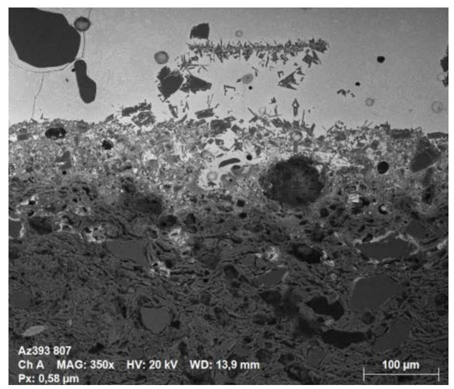

Figure 2. Interface and "centipede".

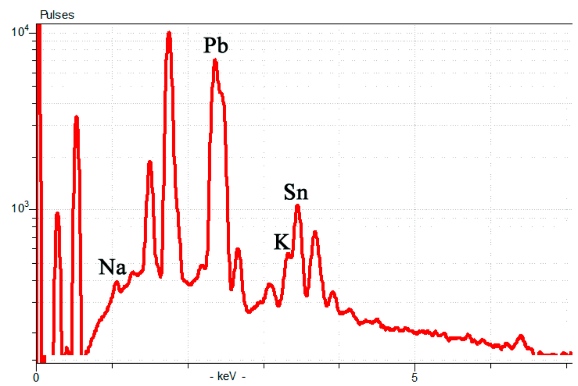

Figure 3. Glaze spectrum depicting in the Na, K, Sn and Pb peaks the characteristics of 16th century Lisbon glazes.

The composition of the glaze is characteristic of what we called "the circle of João de Góis" [2, p. 131], quite unique when compared to contemporary Spanish and Flemish productions because of its relatively low contents in sodium and potassium and high in tin and in lead (Figure 3) with Si/Pb ratios of 0.36 ±0.2 in all samples. It suffices for an attribution to the 16th century workshops of Lisbon.

The composition of the biscuits, with Ca/Si ratios between 0.50 and 0.58 is different from both early panels made of local clay, usually with Ca/Si ratios below 0.35, and panels dated from the first half of the 1590s, with average Ca/Si ratios of around 1.0 [3]. A tentative and highly uncertain attempt to date this panel by the calcium-content of the biscuits, presuming its time-wise increase, would set it around 1590.

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Lead antimonate-based pigments and the colour palette of Portuguese azulejos

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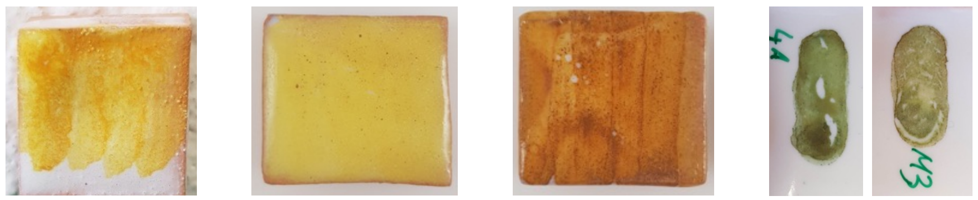
SUMMARY: Using a technical historical approach which combines the chemical analysis of historical tiles with the laboratory replication of pigment recipes, this work addresses the role of lead antimonate within the colour technology of Portuguese azulejos.

KEY-WORDS: Azulejos; SEM-EDS; pigments; technical art history; lead antimonite.

Decorated wall tiles known as azulejos form one of the most important pieces of Portuguese cultural heritage, as well as the country's most original contribution to Europe's artistic heritage. Thanks to multiple influences from Spain, Italy and the Flanders, a local tradition emerges towards the end of the 16th century and quickly becomes widespread [1]. Combining long-lived technological traits with innovation, the chromatic palette of Portuguese tiles went through a period of expansion in these initial decades. Besides white and blue, panels show brown and purple decorations, as well as various shades of yellow, orange and green. But while elsewhere in Europe we have treatises detailing how glazed ceramics were painted and what pigments were employed, the complete lack of such sources in Portugal severely hinders our understanding of artistic practices connected with azulejos.

Thanks to the efforts of heritage and conservation scientists that addressed the issue by turning to the analysis of the tiles themselves, a picture has started to emerge around the technology of tile manufacture [1, 2, 3, 4]. In line with current European practices, a number of metallic oxides were used to achieve the various colours. Among these substances, lead antimonate ($Pb_2Sb_2O_7$) appears to occupy an especially relevant spot. Mixed with various reagents, lead antimonate was found in yellow, orange, brown and olive-green pigments. But what recipes did painters adopt to make their colours? And do these recipes change significantly over time?

Using a technical historical approach which combines the chemical analysis of historical tiles with the laboratory replication of pigment recipes, this work addresses the role of lead antimonate within the colour technology of Portuguese *azulejos*. First, a number of pigments were re-worked following historical *majolica* recipes. These include lead antimonates modified with zinc, tin or iron oxide, as well as a mixture of lead antimonate yellow and cobalt blue. The pigments were then painted on test tiles, over a powdered white glaze, and fired again. The presence and quantity of the different ingredients were found to strongly influence the colour, resulting in a broad spectrum of pigments spanning from pale yellow to dark orange and olive-green (fig.1). This shows how small adjustments to the lead-antimony base provided artists with an extensive palette, thus accommodating their chromatic needs.



Lead antimonate with zinc | Lead antimonate with tin | Lead antimonate with iron | Lead antimonates with cobalt

Figure 1. Some of the replica tiles produced in this work, painted with different lead antimonate recipes.

In order to check our replicas against historical *azulejos*, an assemblage of 16th to 18th-century tiles from the *Museu Nacional do Azulejo* in Lisbon was analysed by scanning electron microscopy (SEM-EDS). Our results indicate that several lead antimonate-based pigments and pigment combinations were used across time. Besides the lead-antimony base, we found evidence of yellow, orange and brown decorations achieved through the addition of zinc, tin and iron, or mixtures of them. As for olive greens, these were always achieved by combining one of the base yellows available with a cobalt blue pigment, a peculiarity restricted to Portugal.

Most importantly, we found that some of our replicas match the composition of historical *azulejos*, allowing us to identify what pigment recipes were used by Portuguese artists, therefore shedding some precious light on the technological and artistic practices at the core of one of Portugal's most renown pieces of cultural heritage.

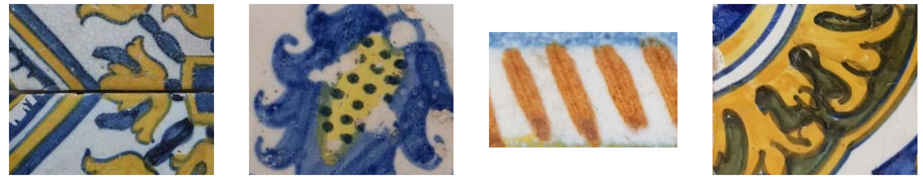


Figure 2. Some of the historical tiles analysed for this study, showing decorations with various shades of yellow, orange and green.

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Synthesis of lead-tin-ash, or calx, by calcination of mixtures of lead and tin oxides

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SUMMARY: The use of lead-tin ash, or calx, as a synthetic ingredient in the production of tin glazes is well attested in archival sources. In recent years, significant efforts have been undertaken to investigate the historical production method of tin glazes by the creation and analysis of glaze reconstructions. Calx was traditionally made by the oxidation of molten mixture of lead and tin metal, a toxic and hazardous process which limits the availability of calx to modern day research. Here we report an alternative synthesis method of calx by the calcination of mixtures of lead and tin oxides in an electrical kiln. XRD-analysis of the synthesized calxes indicate a similar crystalline composition of traditionally prepared calxes, mainly including lead stannate (Pb_2SnO_4). Tin glaze reconstructions using the synthesized calxes show a similar distribution of microcrystalline cassiterite (SnO_2) as the original tin glaze that was replicated.

KEY-WORDS: Lead-tin-ash, calx, Tin glaze, Glaze reconstruction

Lead-tin-ash, or calx, was a key synthesized material used in the production of tin glazes in the Levant from the 9th century CE onwards, and in Europe from the 13th until the late 19th century CE.[1] Its use is well documented in written sources on the making of tin-glazed ceramics, e.g. by Piccolpasso in his famous *Li Tre Libri Dell' Arte del Vasaio* (c1558 CE), as well as surviving documents by manufacturers, e.g. the manuscript recipe book (c1712-1720 CE) by the Dutch tile maker Petrus Sijbeda of Harlingen. Calx was typically produced by the potters themselves by the oxidation of lead and tin metal, melted together in a specific proportion. Historically this was done in a small open furnace especially constructed for this purpose. The melted metal alloy needs to be constantly stirred and, once it begins to form, the white-yellow oxidation powder has to be scraped-off.[2]

In recent years, the historical production method of tin glaze has been investigated through glaze reconstruction experiments. Not all of these have involved the use of calx as this is not a commercially available material and is problematic to produce due to health and safety regulations and concerns. For example, calx has been made by replicating the historical method using an electric kiln, with constant stirring of the molten metal.[3] The formation of the unique microstructure of tin glazes, characterized by microcrystalline SnO_2 (cassiterite) precipitated from the glaze melt, is a direct consequence of the combination of the raw materials used and the complex eutectics these form during firing. In order for glaze reconstructions to reflect the historical production method and the resulting glaze microstructure as closely as possible, the use of calx is an important prerequisite.

In general, a mixture of lead and tin oxide powders have been used to create tin glaze reconstructions. This research reports the synthesis of calx from mixtures of lead and tin oxides (PbO, Pb_3O_4, SnO_2) that have been calcined in an electric kiln, as a safer alternative to the traditional synthesis method. Two mixtures - $Pb_3O_4 + SnO_2$ and $PbO + SnO_2$ - were prepared, having a Pb/Sn-ratio of 2.52 based on a previously studied Dutch tin glaze (Van Oort, Utrecht, c1700-1720 CE).[4] Samples of each mixture were placed on an unglazed ceramic board, and fired in oxidation to temperatures ranging from 600 to 1000 °C (150 °C/hour, 20 minute hold). The crystalline composition of both the starting mixtures and the reaction products were analysed by X-ray diffraction (Figs. 1, 2).

The results clearly show the temperature-dependant formation of lead stannate (Pb_2SnO_4). In the Pb_3O_4-based mixture some PbO (massicot) and some lead stannate have already formed at 600°C. At 700°C and higher all the lead oxides have reacted with tin oxide to lead stannate, and a little tin oxide remains present. In the PbO-based mixture the PbO appears to have changed structurally at 600°C, but the reaction with SnO_2 starts above 700°C and has completed at 800°C, while also here some SnO_2 is left. This is comparable to published XRD-data of calx produced via the traditional method and having a Pb/Sn-ratio <3.5 (the stoichiometric requirement for Pb_2SnO_4), indicating that the synthesis method using lead and tin oxides is a viable alternative.[3] Currently, reconstructions of the tin glaze that provided the Pb/Sn-ratio, and using the synthesised calx samples, are ongoing. The initial results have proven successful in terms of the glaze melting behaviour, opacity and microstructure. SEM-EDX analysis of cross-sections show a similar distribution of cassiterite microcrystals compared to the original tin glaze. This further indicates the applicability of the calx synthesis method developed in this study.

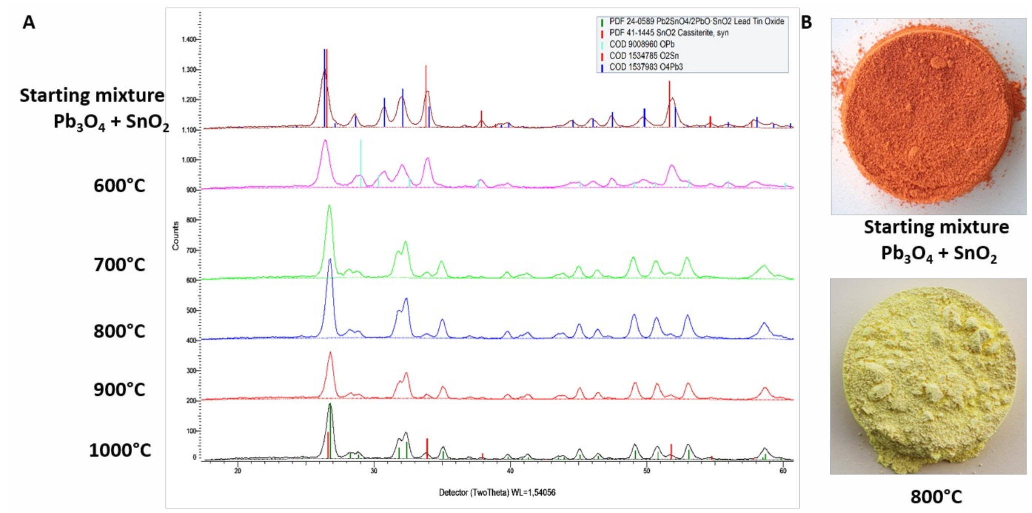

Figure 1. A. Stack plot of XRD diffractograms of the Pb_3O_4+SnO_2 starting mixture, and calcined products fired at 600 to 1000 °C. B. The Pb_3O_4+SnO_2 starting mixture and its calcined product fired to 800 °C.

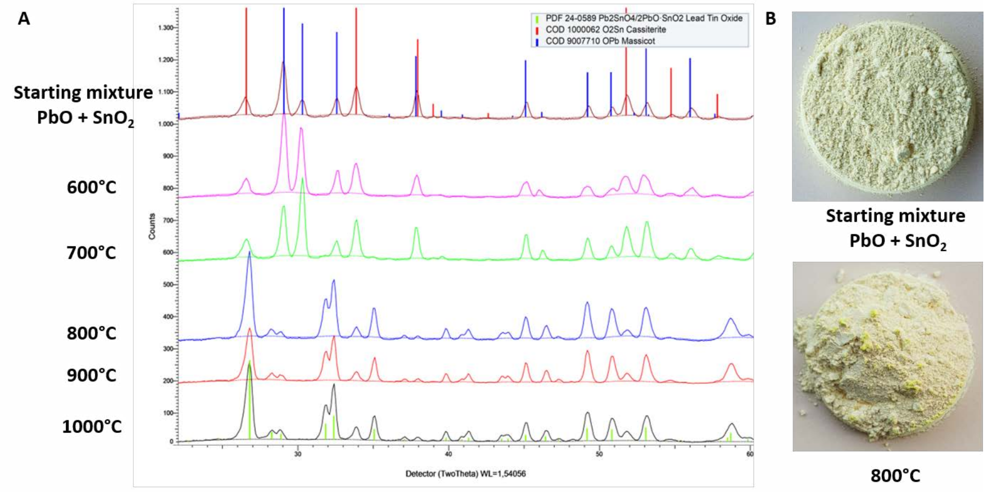

Figure 2. A. Stack plot of XRD diffractograms of the $PbO+SnO_2$ starting mixture, and calcined products fired at 600 to 1000 °C. B. The $PbO+SnO_2$ starting mixture and its calcined product fired to 800 °C.

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Azulejos, urbanity, education and democracy

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SUMMARY: A little square of earth as an instrument of philosophical discourse.

KEY-WORDS: Azulejos; Art; Urbanity, Education; Democracy.

INTRODUCTION

What kind of society do we want? The question is burning today, and each of us is responsible as an actor in society. From the beginning of our respective careers, we choose paths, make specific decisions that lead us to take a position in society. This small painted square of earth, measuring 14 by 14 cm, may seem simple and without apparent meaning in terms of choosing a discourse. However, selecting it as a working base to support architectural works has allowed many individuals to work on immense projects throughout history in Portugal, Spain, France, Holland, Italy, Germany, Morocco in North Africa, the Middle East, South America, China, and Japan. They are just small squares of baked and painted earth. Whether creating pottery in quantity, covering entire walls of churches or mosques, filling underground stations with this painted terracotta material, or turning them into unique art objects of hundreds of copies, this technique fascinates us because it is the oldest industry in the world: baked and painted earth! Just earth accessible to everyone, under our feet.

Democracy

As an artist and architect, when I sought to create immersive spaces fostering social inclusion while crafting monumental urban artworks and aiming to facilitate the participation of thousands of hands and minds, I chose to utilize this small square of earth. Through this humble tile, it became possible to: (1) instruct in an art technique, (2) convey an important philosophical concept of democracy, (3) collaborate collectively in a humanistic synergy, (4) generate heritage urban spaces, (5) foster a sense of permanence, allowing each individual to see themselves mirrored as a citizen. This 2 dm2 painted tile, as tiny as it may be, holds unique significance precisely because of its size. Anyone can grasp it in their hands, enabling individuals of all ages to participate in constructing monumental works and thus becoming active contributors. Over the past 40 years, with the Association “Inscrire”, our team has traversed the globe, inscribing and painting on city walls. With the involvement of thousands of participants, we lay the foundations of democracy, a philosophy of life and thought, increasingly imperiled due to its diminishing presence in educational curricula. This urgency underscores the role of the artists and intellectuals as a unique interdisciplinary social position. Only the azulejo allows for this extravagance: the amalgamation of urbanity, art, and democracy.

A figurative language

If we delve into the history of azulejos and their myriad themes used as decorative elements, such as animals, myths, and various narratives, we can then conceive the idea that thinking, drawing and painting human rights on city walls is possible. It was in Portugal that this concept took root when I completed the Parque metro station, focusing on the dual themes of human rights and the history of Portuguese discoveries. Drawing from my own two-year apprenticeship at the renowned Viúva Lamego factory near Sintra, where, alongside a tribe of artisans, we created 450,000 hand-painted tiles, I envisioned a methodology for teaching fundamental rights dedicated to high school students. This approach allows reflection on a theme as crucial as mathematics, enabling individuals to paint their ideas on a few tiles, and through creative combination, assemble them to form a discourse in figurative images understandable to everyone in public spaces. It's akin to creating a kind of hieroglyphic language, a figurative language that captures attention, crafted by the timeless hands of youngsters on the walls of cities.

Translating a thought into an image

Through the medium of azulejo, we have been able to merge art, human rights education, democratic philosophy, and create works in public spaces. Over thousands of years, language initially took on a figurative form with hieroglyphs, gradually evolving into various abstract alphabets, giving rise to numerous languages with more or less developed written traditions. Interestingly, with the advent of computer science and media, the world is now inundated with rapidly viewed images that, with each click, blend and jostle in our minds. Contemporary society is reverting to a language of images. In this ephemeral environment, azulejos provide us with the means to teach and disseminate, to create and inscribe, enduring and public images of the concepts of democratic philosophy.

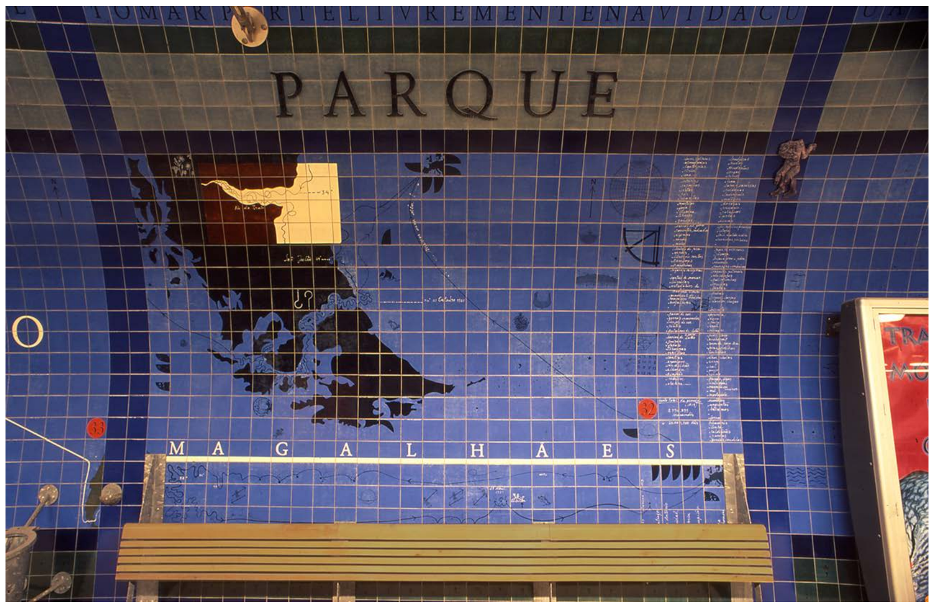

Figure 1. Details of 1 panel out of 50 at *Parque station* in Lisbon by Françoise Schein.

Figure 2. Mural *The way to the human rights* in Brasilia at the subway station *Galeria dos Estados*.

Figure 3. Detail of an article of the Declaration of the Human Rights by a youngster in Brasilia.

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The blackening of porcelain enamel glazes in anaerobic burial conditions: with particular reference to items from the Geldermalsen shipwreck

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SUMMARY: This research concerns a novel example of ceramic glaze degradation; the intriguing occurrence of blackened lead-glaze enamels on Chinese porcelain, specifically from the Dutch ship The Geldermalsen which sank in the South China sea while transporting its cargo to the Netherlands in 1752. The study combines historical documentary research with conservation science and technical art history in order to elucidate the cause of the blackening of the decoration of a number of the items recovered from the wreck site. The shipwreck was discovered and salvaged by captain Michael Hatcher and his crew in spring 1985 and, in April 1986, the items were put up for auction. The sale, referred to by Christie's as the auction of 'The Nanking Cargo', lasted five days and attracted bidders from all over the world. The Christies auction catalogue stated that: "Much of the blue and white porcelain is in almost pristine condition, whereas much of the enamel decoration has become black, silvery grey or degraded to various degrees"[1]. No explanation of the blackening was given at the time nor has the cause been satisfactorily elucidated in subsequent publications.

KEY-WORDS: Chinese porcelain enamel, lead sulfide, marine archaeology

This GlazeArt2024 contribution is the first report to be disseminated on the incidence of this form of deterioration with the Geldermalsen porcelain. It is based on initial research undertaken during a recent University of Amsterdam Master's thesis project[2] which has now given rise to financial support from NICAS (Netherlands Institute for Conservation and Science) enabling the first concerted research programme aimed at understanding this phenomenon. The focus of this contribution is a description of the context and nature of the porcelain lead-glaze enamel deterioration together with preliminary results arising from optical examination and analysis of the degraded surface. An outline of the scope of the forthcoming NICAS project completes the overview of the topic and highlights the decoration and conservation issues which need to be elucidated for a proper understanding of the phenomenon.

Figure 1. Two famille rose plates: on the left with no archeological history (Tennent collection), on the right with blackened enamels from the Geldermalsen (Groningen Museum Inv.1986.0102)

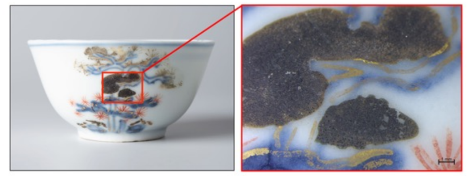

Figure 2. Imari cup with blackened enamel decoration from the Geldermalsen shipwreck (Tennent collection)

This porcelain enamel blackening, as shown in figures 1 and 2, is closely related to the anaerobic microbiological blackening of Dutch 'Delftware' glazes which occurs in terrestrial archaeological environments such as cesspits and canal sediments and has consequently received greater research attention[3,4]. This research demonstrated that the blackening process of these glazes involves the formation of black lead sulfide within the lead-based glaze in a transformation that implicates the presence of sulfate-reducing bacteria in the archaeological sediments. Additional research has shown that this blackening can be totally reversed over a period of weeks by exposure to strong sunlight where both heat and light are involved in the conversion of the lead sulfide to lead sulfate with the consequent recovery of the original glaze appearance[5].

Although the Geldermalsen porcelain burial environment at the bottom of the South China sea is very different from that of a cesspit or canal sediment, sulfate-reducing bacteria are again implicated in the blackening process by the reports of a characteristic 'rotten egg' smell of hydrogen sulfide that was present during the underwater excavations to recover the porcelain items from wooden tea chests[6]. The fact that tea was contained within the chests as a valuable commercial product, with the additional value of cushioning the porcelain, adds to the relevant information which will help understand the deterioration process[7]. Although blackened enamel-decorated Chinese porcelain from marine environments has not been widely reported, examples from the Götheborg and the Vung Tau shipwrecks have been mentioned. In addition, Chinese porcelain sherds with blackened enamels were found in the bed of the Amstel River in Amsterdam[1] and in cesspits at Cistercian Abbey of Clairefontaine in Luxembourg[8]. The occurrence of blackened sherds from the latter two sites indicates that this form of discoloration is not specifically related to maritime archaeological contexts.

The complexity of the degradation process and chemistry has been exemplified by provisional microscopical analysis as well as XRD analysis performed on blackened enamel pine leaves on an Imari cup[1].The results revealed the presence of caracolite ($Na_3Pb_2(SO_4)_3Cl$), in addition to lead sulfate ($PbSO_4$), lead sulfide (PbS), and copper sulfide (Cu_2S). Although the matches in the diffractogram for the latter two minerals were not as definitive as for caracolite and lead sulfate, only the sulfides PbS and Cu_2S can account for the devitrified enamel's black colour. While $PbSO_4$ is unlikely to form in anaerobic conditions, it is known to form post-excavation, due to oxidation of PbS. Another interesting feature that requires further investigation is the observation that zones with red enamel decoration seem to have remained unaffected.

The diversity of degradation products underlines the need for further analytical studies with a wider range of instrumentation (XRF, SEM-EDX, XRD, LA-ICP-MS and XPS) in the forthcoming NICAS project to rationalize the variations in the behaviour of the various enamel decorations present. Experimentation will involve the reconstruction of Chinese enamel recipes together with modelling and reconstruction of the micro-biological deterioration process in the laboratory. The potential for recuperation of the original glaze colours will also be explored by means of exposure to light and high temperature.

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The reversal of lead sulfide blackened earthenware glazes by means of outdoor exposure to sunlight

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SUMMARY: Lead glazes on earthenware can undergo blackening in anaerobic environments as a result of the formation of black lead sulfide within the glaze due to microbiological activity by sulfate-reducing bacteria over many decades. In this article the results of a recent campaign of roof exposure in Lisbon, incorporating environmental data, give a better understanding of the factors which bring about the glaze transformation. Accordingly, the potential for optimising the efficacy of this novel, eco-friendly treatment in the future is enhanced.

KEY-WORDS: Blackened ceramics, Lead sulfide, lead sulfate, Glaze, Earthenware

It is well established that lead glazes on earthenware undergo blackening in anaerobic environments such and canals and cesspits as a result of the formation of black lead sulfide within the glaze due to microbiological activity by sulfate-reducing bacteria over many decades (1, 2). Conservation treatments can result in successful recovery of the original glaze appearance by transformation of the lead sulfide (PbS) into white lead sulfate ($PbSO_4$), but chemical treatments are often only moderately effective and at other times aggressively deleterious. It has been shown that exposure to strong summer sun over several weeks can result in an even more impressive recuperation of the original state of the glaze (3), as illustrated in Figure 1.

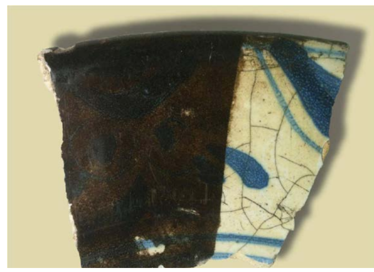
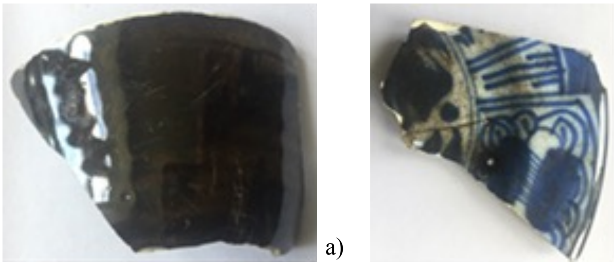


Figure 1. Fragment of blackened Delftware (c. 1660-1680, found in Amsterdam) illustrating recovery of the original glaze design in the right-hand portion which was exposed to Lisbon summer sun for 12 weeks.

More recently, a colour science rationalisation has been presented to explain how transformation of black lead sufide particles to white lead sulfate results in recuperation of a transparent lead glaze, thereby resulting in the reappearance of the coloured glaze design which had been obliterated by the formation of lead sulfide during burial (4). In this GlazeArt2024 contribution, the efficacy of the recuperation of the glaze appearance by sunlight is further scrutinised. The results of a recent campaign of roof exposure in Lisbon, incorporating the environmental data for ultraviolet light, visible light and temperature at the weathering station, give a better understanding of the factors which bring about the glaze transformation and, as a consequence, can be optimised for maximum efficacy of this novel, eco-friendly treatment process in the future. This research concerns the roof exposure of two fragments of lead sulfide blackened Delftware ceramics (Figure 2) to the strong sunlight of the roof site of the National Civil Engineering Laboratory (LNEC). These fragments illustrate the range of blackening which occurs; ultimately it can obliterate the glaze design.



a) b)

Figure 2. Delftware ceramics blackened by lead sulfide prior to strong sunlight exposure. (Fragment samples courtesy of Owen Ooievaar.)

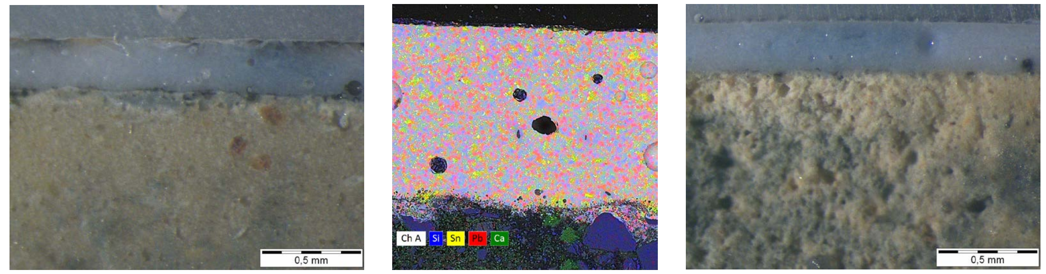
The programme ran for a total of 105 days, from 28 July to 9 November 2023, with approximately monthly photographic documentation. Half each ceramic fragment was covered by aluminium foil and the samples were exposed on a south-facing rack at an angle of 45 degrees to the horizontal. The results of this exposure period are shown in Figure 3.

Several fascinating features concerning the glaze recuperation process are evident. Most significantly, the glaze appearance on the portion not covered by foil has been very successfully

a) b) c)

Figure 3. Effect of strong sunlight on blackened Delftware ceramics. a) and b) recovery of the original glaze design in the right-hand and lower half, respectively, where sunlight was not occulted by an aluminium foil layer, c) reverse of the second fragment where the effect of the transparent tape which was securing the aluminium foil can be observed.

recuperated with the recovery of the vibrant blue and white glaze colours and the retention of the smooth, glossy surface sheen. (After 39 days the reduction of the blackening had almost reached that of the full exposure period.) More unexpected, and in contradiction to the previously-reported example (Figure 1), is the observation that the glaze blackening under the foil has also been somewhat ameliorated (Figure 3a). Even more intriguing are two additional observations. Firstly (and not illustrated), the glaze blackening on the uncovered area of the reverse side, which was not receiving direct sunlight, has also reverted to a considerable extent. Secondly, the Scotch adhesive tape, which haphazardly covered the reverse side to secure the metal foil, has clearly inhibited the reversion process (Figure 3c). This effect is also partially visible under the narrow strip of adhesive tape adjacent to the foil on the upper surface of the first fragment glaze (Figure 3a).



a) b) c)

Figure 4. Cross section images of the first fragment. a) Optical microscopy of the blackened glaze surface; b) SEM-EDS map of the blackened glaze layer; c) Optical microscopy of the sunlight exposed glaze surface.

The optical microscopy of the embedded, polished cross-sections reveal a distinct black line not only at the glaze surface but also at the glaze/body interface (Figure 4a), both of which disappear after sunlight exposure (Figure 4c). Though two zones of glaze conversion to lead sulfide are present, no clearcut confirmation by SEM-EDS was obtained; the thinness of the sulfide layer and the dominance of lead as a major glaze component result in no confirmatory sulfur signal from within the thin degradation layers (Figure 4b). Nonetheless, the uniform glaze composition indicates that in both these fragments no superficial high lead 'coperta' (in Dutch, *kwaart*) secondary layer, sometimes applied, is present in these samples.

These observations, in conjunction with the environmental data obtained during the exposure period, give rise to some preliminary conclusions on the oxidation process. Photochemical oxidation is clearly involved, but the role of temperature is now also apparent and needs to be taken into account. In addition, the inhibiting effect of the clear adhesive tape requires further investigation in order to pinpoint its role; it could be acting as a filter to light or as a barrier to atmospheric oxygen and/or moisture.

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Preservation of tangible musical cultural heritage - an interdisciplinary approach. “Ratinhos” faience plates under focus

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SUMMARY: In this communication we present our first analyses carried out in the frame of the on-going exploratory project SuitNanoMusic (IN2PAST). This project combines multidisciplinary knowledge of Technical Sciences, Musical Iconography and Humanities & Social Sciences. The project aims to trigger an interdisciplinary discussion on the suitability and acceptance of new emerging (nano)/materials for preservation of tangible musical heritage. Its main objectives are to determine the suitability and efficiency of novel materials for the preservation of ceramic traditional artefacts and musical instruments and to reveal the musical, socio-cultural and historical narrative behind them, their function and manufacturing. We will discuss our project and demonstrate preliminary data from the case study of "Ratinhos" faience plates.

KEY-WORDS: Cultural heritage, Faience, Plates, Pigments, Socio-cultural narrative

Musical instruments and musical iconographic sources, e.g., in decorative arts, paintings and sculptures, are among the main musical assets that constitute tangible musical heritage. They are an integral part of the cultural, historical and environmental context in which they are situated and, likewise other cultural heritage objects, suffer degradation issues. Therefore, music-related assets also deserve particular attention in terms of diagnostics, conservation and restoration, where all settings and social contexts should be preserved with respect to authenticity and sustainability principles. The state of any of their individual components requires a multidisciplinary awareness of a very large context [1].

Museu Nacional da Música has a group of ceramics objects, comprising a large range of traditional musical instruments and decorative objects with representations of musical iconography (decorative or tableware plates, figurines, decorative musical instruments) (Figure 1) [2]. These items were produced with different ceramic materials & techniques. Within the collection there is a considerable ensemble of faience plates depicting musicians and dancers. Some were produced in Coimbra, commonly designated as “Ratinhos” [3] that have been objects of studies in the frame of our on-going exploratory project SuitNanoMusic: Suitability of nanomaterials for preservation of tangible musical cultural heritage (N2PAST). The nickname “Ratinhos” was given to rural workers that would seasonally migrate from Beira to Alentejo regions to work in the harvest. It is believed that the workers used to bring such plates for their meals. The plates date from the end of 19th and the first decades of 20th century. Our first set of studies of “Ratinhos” plates presented in this communication include non-invasive techniques, such as technical photography, hyperspectral imaging, colorimetry and h-XRF spectrometry. Combined with analysis carried out at the museum, our interdisciplinary scope also includes carrying out ethnographic interviews with rural workers, on the cultural meanings of the ceramics.

Figure 1. Front view of a faience plate “Ratinho” with woman playing English guitar, Coimbra (19th-20th century). Collection of the National Music Museum.

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The life and afterlife of the Adès collection of medieval Persian glazed ceramics

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SUMMARY: Intact pieces of glazed ceramics at museums may have represented the missing links to understanding the emergence of glazed tableware as a global commodity during the medieval period, but this rich body of evidence remains largely untapped. The intactness of museum pieces has prevented the application of scientific analyses – which are mostly invasive in nature – to gain more insights into their provenances and technologies. This information can in turn be fed into expanding the contexts of museum pieces. How can we extract more information from these intact museum pieces? How can we bridge the gap in approaches to studying fragmentary archaeological materials and intact museum pieces? We will tackle these questions using the Adès collection of medieval Persian glazed ceramics as our case study.

KEY-WORDS: Glazed ceramics; medieval period; Persian; lustre; museums.

The Adès collection consists of over 100 pieces of glazed ceramics, which are mostly made up of lustre ware but also other ware types such as mina'i and turquoise glazed ware, held in six museums across the UK (Fig. 1). These pieces are purported to have belonged to the mysterious 'Gorgan Finds' – a hoard of glazed ceramics dating to the late 13th century CE that were recovered from large urns in the city of Gorgan, modern Iran [1]. The provenances of the Gorgan Finds are yet to be determined, which mirror the current state of debate revolving the origins and craft organisation of medieval Persian glazed ceramic production [2, 3, 4]. It is against this background that we develop an interdisciplinary project entitled '*The Life and Afterlife of the Adès Collection of Medieval Persian Ceramics*', bringing together scientists, archaeologists, pottery artist, conservators and museum curators, to reconstruct the journey of the pieces of the Adès collection [5, 6]. Through this process we will also establish a novel, non-invasive analytical protocol, which we hope will be applicable for other materials.

We conducted analysis on the pieces at the Fitzwilliam Museum, University of Cambridge, which holds the largest quantity of the Adès collection, using techniques including UV light, optical coherence tomography (OCT) and portable x-ray fluorescence (pXRF). Preliminary results showed that the technologies used are consistent with the known contemporaneous examples of medieval Persian glazed ceramics. Most pieces have a stonepaste body, made of crushed quartz, glass and clay. A high zirconium concentration is identified in the body of some pieces, which may have resulted from using the glass made in Gorgan [7], suggesting the presence of multiple workshops, with some based in Gorgan. This finding coincides with the stylistic analysis, which highlights the presence of various artisanal signatures. Two main types of glaze were used: a clear one that has a low lead and tin concentration and an opaque one that has a high lead and tin concentration. A variety of pigments was used, ranging from a combination of copper, silver, chromium and iron oxides. The variation seen in the colour of the lustre decoration was likely caused by varying firing atmospheres, which we tested through a series of firing experiments (Fig. 2).

Figure 1. A lustre ware of the Adès collection from the Oriental Museum, Durham University (photo taken by Carmen Ting).

Figure 2. The lustre-firing kiln we reconstructed as part of our replication experiment at the Fitzwilliam Museum, University of Cambridge (photo taken by Carmen Ting).

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The technology of polychrome glazed ceramics in Tunisia: new data from the site of Chimtou

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SUMMARY: Ifriqiya was one of the earliest production centers of polychrome glazed ceramics in the Islamic territories of the Central and Western Mediterranean. This began as early as the 9th century during the Aghlabid period, when yellow, green and brown glazes were applied over a painted and often white background. Tunisia is traditionally believed to have acted as a diffusion centre for ceramic glazed technologies into other regions of the Western Mediterranean, such as Sicily, while it has been recently suggested that in al-Andalus glazed wares developed independently. However, due to the lack of analysis and comparative data on Tunisian glazed ceramic, its role in technology transfer is still poorly understood. Here, we present preliminary chemical and petrographic analyses of 30 polychrome glazed ceramics from a medieval village at the site of Chimtou, Tunisia, dated to the 10th-11th century. The results shed new light on the technology employed in the manufacture of glazes and the bodies, thus contributing to our understanding of ceramic production and technological transmission in the Central Mediterranean.

KEY-WORDS: Ceramic technology, Glaze technology, Tunisian ceramics, Scanning electron microscopy, petrography

In Ifriqiya, the production of polychrome glazed ceramics started as early as the 9th century during the Aghlabid period, when yellow, green and brown glazes were applied over a painted and often white background [1], [2]. Their production represents a notable departure from the previous ceramic traditions, which required not only the adoption of glazing technologies but also the embracing of new shapes and decorative styles by the local populations and consumers. Ifriqiya is traditionally believed to have played a prominent role in the diffusion of glazed technology to other Islamic territories of the western and central Mediterranean. The nature and direction of this technological connection has been at the centre of academic debate in current scholarship [3]–[6]. The aim of this paper is to provide new insights on the technology of polychrome glazed ceramics in Ifriqiya through the study of a glazed ceramic assemblage dated to the 10th-11th century from the archaeological site of Chimtou, in the Medjerda Valley. In this study, scanning electron microscopy energy-dispersive spectrometry (SEM-EDS) and thin-section petrography are used to identify the technology employed for the manufacture of the glazed ceramics, including the type of raw materials used, the preparation method of the glaze and the body, the method of application of the glaze, and the possible provenance of the ceramics.

SEM-EDS analysis of the ceramic bodies reveals that they are all made with calcareous clay, with variable CaO contents ranging from 12 to 33%. The ceramic bodies are also characterised by relatively high Fe_2O_3 (4-7%), moderate Al_2O_3 contents (10-16.5%), low K_2O (<1.4%), significant levels of Na_2O (1-2%) and MgO contents at around 2%. Under the SEM, the samples show round to angular quartz grains as the main inclusions, elongated voids associated to the shrinkage of the body during drying and firing, as well as numerous voids after decomposed $CaCO_3$ inclusions to CaO. The ceramic bodies also contain relics of foraminifera microfossils, rare feldspars and heavy minerals. Petrographically all samples are characterised by a similar mineralogical composition, including mainly rounded, subrounded to angular monocrystalline quartz, rare feldspars, iron-rich nodules and sandstone as well as abundant calcite inclusions which are often decomposed. While nature of the inclusions is the same in all of the samples, some differences in the amount, distribution and size of inclusions can be observed which allow us to divide the samples into three main petrographic groups and one sub-group. The mineralogical and textural characteristics of the samples suggest a Tunisian origin. Indeed, comparable fabrics are found at Raqqada and Sabra al Mansuriyya [7], while the predominant presence of round quartz, calcareous inclusions and microfossils is consistent with the use of calcareous fossiliferous clay from central Tunisia (i.e Kairouan) [8]. The different fabrics identified can thus be indicative of the presence of different workshops which were active in the region.

The chemical analysis of the glazes indicates that there are two main types of glazes: one group of samples is of a high lead intermediate alkali type, with variable alkali contents which do not exceed 4%, and a lead alkali type with lower contents of lead oxide between 30% and 50% as well as higher levels of alkali between 4% and 7%. In terms of colourants employed, the yellow glazes have been obtained by adding iron oxide (1-3% Fe_2O_3), while the green glazes have been coloured with copper (1-3% CuO) completely dissolved in the glaze. The brown glazes and brown decorations have been made using manganese in variable quantities (0.4-8%). A light green glaze was due to the combination of few amounts of Fe_2O_3 and CuO, while turquoise is obtained adding copper to a glaze containing some alkalis.

Interestingly, virtually all the transparent glazes reveal the presence of very rare and small particles rich in SnO_2, PbO, and sometimes Sb_2O_5, which often results in low concentrations (<0.8%) of these oxides in the glaze. Given the rare occurrence and small size of the crystals, their intentional addition as opacifiers can be excluded. We propose that tin oxide and the tin-antimony compounds have been introduced using scrap metals as a source of lead, such as Roman lead pipes (fistulae acquariae) which were joined with a Pb-Sn solder and which also contained antimony as an impurity [9], [10]. Particularly remarkable is the finding in sample Chi 3 of an inclusion showing large irregular grains of wüstite (FeO) dendrites. This is likely to be a slag derived from the smelting of iron ores, suggesting a close connection between glaze making and metallurgy.

Opaque glazes were opacified with cassiterite particles, this time clearly visible under the SEM and more numerous. Our samples are dated to a relative wide time range from the 10th to the 11th centuries and therefore it is impossible to test the hypothesis put forward by Salinas and colleagues [11], [12] regarding the introduction of tin to Tunisia by the Fatimids from Egypt in the late 10th century. However, one sample appears to have been opacified using lead stannate. Lead-stannate was initially used in Egypt and Syria in the 7th and 8th centuries and later this technology spread into Iraq in the 9th century and advanced eastwards in Iran and Central Asia in the 9th-10th century and beyond [13]. In contrast, in Egypt there was a shift to the use of lead-antimonate in the 9th-11th centuries, which appears to have been also adopted in Tunisia in the 11th century [11], [14]. In this context, even though based only on one sample, the finding of a glazed ceramic in Chimtou coloured and opacified using lead-stannate is particularly remarkable and might point to a very different story on the origin of a tin-based opacification technology in North Africa.

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Samarra tiles: focus on the first glazed architectural ceramics in the Islamic world

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SUMMARY: The study focus on 9th century tiles from Samarra, the earliest architectural ceramics in the Islamic world.

KEY-WORDS: Samarra, tiles, Islam, excavations, luster

In the 20th century, tiles were discovered in Samarra, Iraq, the ephemeral capital of the Abbasid caliphate from 836 to 892. To date, they are the oldest tiles in the Islamic world, discovered in a unique example of a preserved 9th-century Islamic city [1]. They were found in the Dār al-Khilāfa, the caliphal palace built for the caliph al-Muʿtaṣim, but the important site spreading over an area of 173 acres, 75 miles north of Baghdad on the Tigris Riverbanks, is little excavated [2]. Various archaeological campaigns between 1910 and 1989 discovered glazed ceramic tiles, but the Islamic site remains unexcavated for more than 80% [3].

The archaeological material was scattered by wars, political crises, as different States were involved in its exploration since the first excavations in 1910 directed by the young French architect Henry Viollet [4]. Moreover, the archaeologists didn't record all the artefacts they found. The excavations in Samarra at the beginning of the 20th century were considered by Ernst Herzfeld, director of the German archaeological mission between 1911 and 1913, to be the first scientific excavations of an Islamic site [5].

Figure 1. Luster tile fragment. Earthenware, polychrome luster painted decoration on opaque white glaze, Samarra (Iraq), 9th c. (27,5 x 20,4 x 3,5cm).

Nr. Sam 785 a Museum für Islamische Kunst Berlin. © V. Rose

For the first time, it was possible to study the Samarra tiles in their whole, by collecting an important and representative corpus from these successive excavations. Today, the set consists of more than 370 fragments. Most of them are in many famous and historic collections around the world [6]. The collected tiles can be divided into three main decorative groups. The most famous is the group of polychrome lustred tiles with different iconographies: mottled, bird's representation, vegetal scrolls. The second is dark brown lustre on a white opaque ground. The last are the monochrome honey-yellow and monochrome green square tiles. Some small groups and single specimens have also been identified as a blue and white one. The study of the collected tiles highlights the issue of the first tiles in Islam in the 9th century and the beginning of the invention of metallic lustre on ceramics, a highly complex technique that developed in several stages during the Abbasid period and spread during the following centuries. Their techniques, iconographies, artistic and historical backgrounds reveal the characteristics and issues of a production linked to the caliphal city of Samarra and the setting of the palace [7]. We will discuss these issues, the invention and development of this technology, its origins, its use and its impact beyond the Abbasid Caliphate. The second corpus of glazed architectural ceramics in Islam, all in the lustre technique, is the setting of the mihrab of the Great Mosque of Kairouan, Tunisia, known as a gift of the Abbassid Caliph, shipped from Mesopotamia to the Aghlabid Emirate in 862 [8], reflecting the reputation of this art. These two corpora will be compared.

From Samarra, the taste and technique of tiles spread across space and time, and they remain a distinctive artistic medium of the Islamic world. A corpus that also highlights the whole historical process from excavation to exhibition.

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Gharb Al-Andalus glazes from the Castle of Palmela: a non-invasive multianalytical archaeometric approach

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SUMMARY: The Islamic presence in the Iberian Peninsula between the 8th and the 13th centuries in Portugal and until the 15th century in Spain, known as Al-Andalus [1], left important technological traces in the ceramic manufacturing practices [2]. A group of 18 ceramic fragments were studied without resorting to sampling. Techniques used included Optical Microscopy, Colourimetry, portable X-Ray Fluorescence and Scanning Electron Microscopy with Energy Dispersive Spectrometry, to provide the material characterization of Palmela's glazes and deliver clues for social interpretations of these societies.

KEY-WORDS: Islamic glazes, Castle of Palmela, Al-Andalus, Archaeometry

The occurrence of glazed ceramic in the Iberian Peninsula is strongly connected with the Islamization process, as it is with the Islamic presence that glazes became an essential part of daily life. The earliest glazes found in the Iberian Peninsula are usually small vessels decorated with green and/or honey-brown glazes from the southern part of Al-Andalus and date from the mid-9th century [2]. The Castle of Palmela, due to its strategic location, was a hub of trade, communication, and defence. In this study, 18 ceramic fragments found during the archaeological works were archaeometrically studied to achieve their material characterization and help unveil manufacturing practices employed by this society. All samples were retrieved from galleries 4 and 5 of the Castle of Palmela and are dated from the 8th to the 11th centuries, the period of Islamic occupation in Palmela before the *Reconquista.* The samples are of monochromatic glazes with green, dark brown and honey colours and a smaller group of 4 samples with bichromatic green and honey glazes. Optical Microscopy (OM), Colourimetry, X-Ray Fluorescence (XRF), and Scanning Electron Microscopy with Energy Dispersive Spectrometry (SEM-EDS) were employed in the study of all fragments, without sampling.

RESULTS AND DISCUSSION

OM observations showed that the fragments found at Palmela's Castle appear in notable conditions despite their long permanence underground, showing only some crackling and corrosion. This, coupled with the reduced size and frequency of inclusions present in the glaze, are a strong indication of an outstanding raw materials preprocessing and technique in its application. The glazes' chemical composition showed that all samples are of lead-based glazes (~ 49 wt.% PbO), with compositions displaying strong coherence with glazes from the beginnings of the Islamic occupation found in the Vega de Granada region (Southeast Spain) [2]. Furthermore, it was seen that all fragments, except for the brown colours, present the typically responsible elements for each observed colour, namely, yellowish colours are coincident with higher iron contents and the green glazes show higher copper contents [2]. To investigate a probable connection between the observed colour and its respective chemical content, a chemometric approach was employed. First, a HCA was performed using the obtained colorimetric data, allowing to establish the separation of samples into three colour groups: green, yellow, and brown. Subsequently, a PCA was employed resorting to the obtained quantifications of the colouring agents present in the glaze composition: Fe, Cu, and Mn. After the statistical analysis, it was possible to determine three distinct groups showing that yellow samples have higher contents in Fe, green in Cu, and brown is a result of the addition of both copper and iron in the glaze.

CONCLUSIONS

The remarkable conservation state displayed by the studied fragments in addition to the fact that several colours and distinct glaze recipes coexisted in Palmela, demonstrates the vast knowledge and consideration that these peoples had for ceramic glazes as it is an outcome of good and careful manufacturing practices. Additionally, the solution found in Palmela for brown glazes, different to the common practices found in other Al-Andalus locations, indicates a local production, but further studies are needed to assess this question.

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Different blues, different painters. Study and comparison of the 18th-century *azulejo* panels from the Lisbon Academy of Sciences

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SUMMARY: This work provides a multidisciplinary characterisation of the 18th-century azulejo panels at the Lisbon Academy of Sciences, in Lisbon. The methodology combined in situ portable XRF and colourimetric analysis with SEM-EDS analysis of polished cross-section samples. Results are discussed in combination with known historical data.

KEY-WORDS: Azulejo; Glaze; Cobalt blue; Glazed tile; In situ *analysis*

The Lisbon Academy of Sciences occupies part of the former Convent of *Nossa Senhora de Jesus*, of the Third Order of St. Francis. The 18th-century renovation of the cloister is well explained on the pillar W/S, mentioning the completion of the works, including the tilework, in 1715. There is some archive documentation as well. However, this does not make it easier to understand the different remaining *azulejos*, and "who did what". It is known that there was a first intervention in 1712-13, paid to the tiler António de Abreu, and in 1713 there was a payment to the painter António de Oliveira, certainly António de Oliveira Bernardes [1]. In 1714, another tiler, António de Oliveira, was hired to continue the work, covering two and a half wings of the cloister, as one had already been completed. This document mentions that the previous campaign shows different mistakes that should now be avoided, both in terms of the quality of the tiles and the laying, explicitly stating that the tiles should be "of a good blue colour". The payment records also show that the tiles were supplied by the potter Francisco dos Santos. On top of that troubled process, since then tiles have been extensively intervened – there are 18th-century restorations, replicas, and so forth.

At this time, Portuguese azulejo was going through its "golden era" – the "blue-and-white" period or the Masters' Cycle (*Figure 1*). Authorship issues have been addressed within the Art History field [*e.g.*, 1,2], although many azulejo panels remain without a secure author. The collaborative process within the workshops has also been considered to address the different roles involved in the production process. More recently, material characterisation studies have contributed to a better understanding of the materials and techniques used in Portuguese azulejo workshops [*e.g.*, 3,4]. By combining these two approaches, we can further advance the knowledge of painters' techniques and workshop practices and, hopefully, unveil current authorship and provenance questions.

This study intends to provide new data through a multidisciplinary approach that correlates historical and visual information with the material characterisation of the azulejos from the Lisbon Academy of Sciences. Other decoration campaigns until the 20th century were also considered and characterised. The methodology combined *in situ* analyses by portable X-ray Fluorescence (p-XRF) and colourimetry (CIE L*a*b*) with laboratory analyses of polished cross-section samples by µ-Raman spectroscopy and Scanning Electron Microscopy with Energy Dispersive Spectroscopy (SEM-EDS). For the latter, samples were collected only from tile fragments in storage. This methodology is part of a wider project focused on the identification and characterisation of the chromatic palette used in 16th- to 18th-century azulejos (ChromAz) [5]. Results will be discussed considering the different sets of panels, their colour shades, and the chemical and morphological characteristics of their *azulejos*.

Figure 1. 18th-century blue-and-white azulejos, cloister of the Lisbon Academy of Sciences (photo by Libório Manuel Silva / *Az Infinitum*)

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The conservation of an early 17th century tin glazed tiled stove from Schloss Hellbrunn, Salzburg

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SUMMARY: This case study describes the conservation intervention of a 17th century tin-glazed tiled stove, which took place between 2019 and 2022, at Schloss Hellbrunn in Salzburg, Austria. The project was closely overseen by Austria's Federal Monuments Authority (BDA) as well as the Palace stakeholders. This intervention was awarded in 2023 the Nigel Williams Prize by ICON, The Institute of Conservation, UK.

KEY-WORDS: Tiled stove; Structural reinforcement; Polyvinyl butyral putty.

Figure 1. Grout damages detail.

This case study describes the conservation intervention of a 17th century tin-glazed tiled stove, which took place between 2019 and 2022, at Schloss Hellbrunn in Salzburg, Austria.

The stove presented severe damage. The most evident was the ongoing blistering and loss of glaze, as well as fractures along the grout lines and on some ceramic elements. This loss of ceramic glaze was mainly due to variations in temperature and humidity in the exhibition room[2]. Environmental analysis previously done[3] showed that there was a huge variation in temperature between the inside and outside of the stove[4].

In 2019 two likely causes for structural fractures were identified: a) the movement of the building and wooden floor beams, and b) the occasional damage caused by maintenance procedures and attempts to gain access to the back of the stove.

A study of the floor's vibrations done in July 2020 concluded that the stove was susceptible to the movement of under-floor beams, resulting in some of the damages. As a result, in December 2020, a more in-depth analysis of the floor and structure under the stove was made and in March 2021, the structural reinforcement of the underfloor beams was carried out.

The conservation intervention primary goal was to reinstate the object's stability but also consider its aesthetic values, allowing the public to fully enjoy its artistry, including the numerous, previous conceived repairs, severely aged but with historic value which needed to be preserved.

Given the stove's history of poorly documented repairs, the choice of materials for this intervention had to be carefully pondered, ensuring the compatibility with old materials, great ageing properties, stability in an uncontrolled exhibition environment, and that they be easily identifiable in the future.

The conservation intervention in the object had a duration of four months, between November 2021 and March 2022. Begun with stabilising fragile and hollow glazed surfaces, followed by revealing the edges of each ceramic tile, uncovering original glazed surface obscured by mortar and overpaint. After achieving this clear view of the gaps and glazed surface, it was possible to start the filling process.

A workshop-prepared putty, with polyvinyl butyral (PVB) as a binding medium, bulked with washed sands and mineral aggregates (glass micro balloons and fumed silica) was selected to fulfil the gaps. Coarser mixtures were applied to large and/or deep spaces and a finer mixture to more superficial losses[1]. PVB putties are lightweight, have good adhesion between layers allowing successive applications and are easily levelled with an ethanol-wetted spatula during application, minimising sanding after drying, as well as the possibility of retouching with acrylics [5].

All new fills were retouched with Golden® acrylic paints and mediums, which are reversible without impacting the fills underneath in case further research must be done. All new glaze and grout fills were toned to the nearest glazed surface, and grout lines with previous painted decoration were sympathetically repainted to highlight the tiled stove as a whole, following its original purpose.

Figure 2. Cleaning Process.

Figure 3. Mortars removal.

Figure 4. Before and after detail of the front ceramic tile.

Conservators in the age of social media can sometimes fall in the trap of judging their project's success by the ability to show striking before-and-after images. The tiled stove at Hellbrunn Palace demonstrates the value of in-depth conservation at its most fundamental level – to preserve the object, from the inside out, looking at its material and immaterial values, ensuring it continues to please and educate present and future generations.

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Old azulejos through new lenses: Integration of digital and non-digital methodologies for the assessment and monitoring of azulejo panels decay

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SUMMARY: This work presents a methodology, involving a highly interdisciplinary team, for documenting, assessing, and monitoring the azulejo heritage with a special focus on its degradation. The azulejos of the façade of LNEC Congress Centre are used to exemplify some results of the proposed methodology.

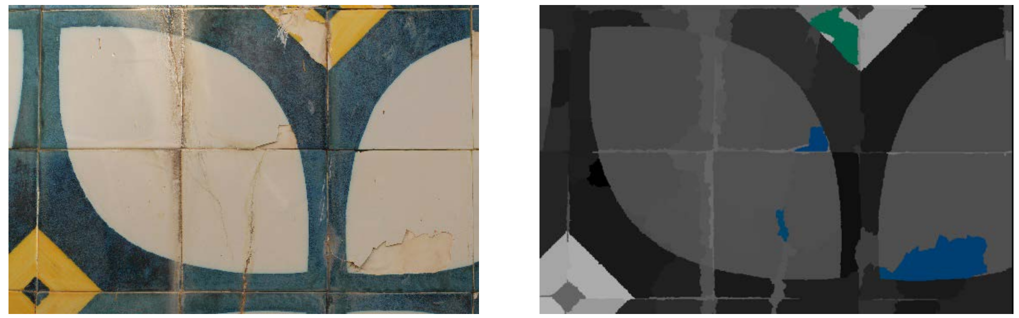
KEY-WORDS: Azulejo; decay; characterization; photogrammetry; digital image processing; Infrared Thermography, GIS.

METODOLOGY FOR AZULEJO DECAY CONTROL

Azulejos are one of the most remarkable Portuguese contributions to cultural heritage, their conservation is therefore of utmost importance. This work proposes a methodology for digital documentation, assessment and monitorization of architectural azulejo, with a special focus on their conservation condition. The methodology is intended to be applied to all azulejos, when there is a will to keep them safeguarded but integrated in their current architectural location.

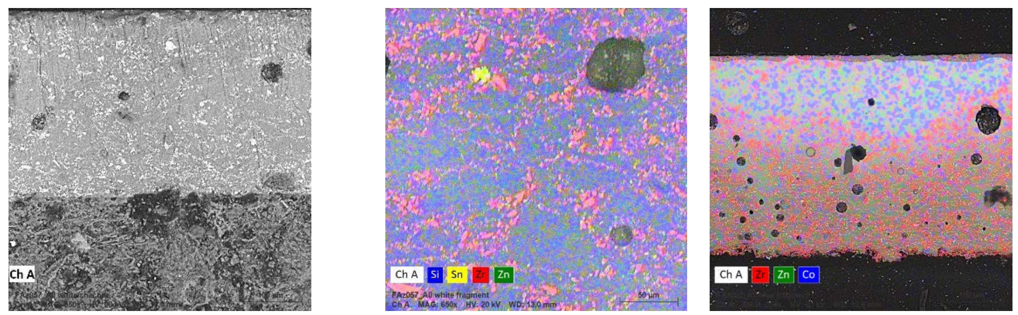
The proposed methodology involves obtaining information regarding the azulejo's history, the building where they are integrated, the materials used (azulejo and mortars materials), their conservation treatments and decay. The azulejos information will be collected *in situ,* researched in archives (e.g. the Gulbenkian Foundation and the National Tile Museum), databases (e.g. AzInfinitum), analysed in the conservation reports (when existing), and extracted from other relevant bibliographic sources with information from the past and present condition of the tiles.

Photographs depicting the conservation state over time are used to obtain an indication of the visible decay rate. Information regarding the probable causes of decay is also collected through surveys to the owners, persons in charge or other entities that may have knowledge regarding the azulejos and building conditions that may have affected the panels. A 3D digital twin of the actual state of the tiles is obtained through photogrammetry, where the correspondent orthophoto is retrieved. This orthophoto will be assessed through digital image treatment methodologies (using eCognition software) [1]. Neighbour image pixels are organized into objects, through a segmentation procedure. The analysed colour and shape properties of the objects allow the distinction between sound and defect objects, enabling the mapping of the damaged azulejo areas (Figure 1). Additional layers of information to aid in the understanding of possible decay factors can be collected via thermal imaging (infrared thermography), ground penetrating radar (GPR), and hyperspectral photography. For information regarding the micro-morphology, mineralogy, and elemental chemical information of the tiles, non-destructive (XRF) and/or micro - destructive analysis (SEM-EDS XRD) (Figure 2) which imply the removal of small tile samples is performed. All the information obtained will be tentatively correlated with the tiles decay.



a) b)

Figure 1. LNEC's congress centre azulejos. a) detail of an azulejo's area with glaze lacunae, b) image depicting a radiometric index where glaze defects are coloured in blue and green.



a) b) c)

Figure 2. SEM-EDS cross section analysis of LNEC Congress Centre azulejos. Morphology, composition and distribution of glaze and biscuit elements: a) white glaze layer and tile biscuit: b) image detailing the dispersion of the zirconium based opacifier crystals in the glaze matrix: c) cross section of a blue painted glaze tile area showing the distribution of the cobalt-based pigment in the glaze layer.

The information collected is also intended to increment the one existing and be made available in related databases, such as AzInfinitum and DB-Heritage. It is also meant to be integrated into GIS (Geographic Information System) and HBIM (Heritage, Building Information Modelling) methodologies [2]. This strategy will therefore allow gathering and sharing the relevant data on the characterization, history, and conservation state of the azulejos and mortars, which can thereafter be used in the design of conservation treatments and for the monitoring of the panels decay rate in time.

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Characterization of 19th-century ceramic objects and paint materials produced by the Portuguese Royal Family

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SUMMARY:

A multianalythical approach was used to investigate the ceramic paint materials and ceramic objects produced by members of the Portuguese Royal Family during the late nineteenth century.

KEY-WORDS: Ceramics, Colorants, HIS

Nineteenth-century ceramic objects decorated with flower bouquets, fables or animals scenes can seem naïve and unsophisticated at first glance. However, the fashion of painting ceramic objects, often referred to as china painting, emerged as a result of the technological advances in the ceramic and glass industry [1] at a time when ceramics were perceived by Western culture as a symbol of industrialiation, scientific knowledge, erudition, and luxury.

The dissemination of this new artistic medium was assisted by the emergent globalization and the organization of numerous world fairs during the last decades of the nineteenth century. Painting on ceramic objects spread rapidly through the European, American, and Australian upper classes, reaching professional and amateur artists [1–3]. This new artistic medium was launched in Portugal amid the Royal Family's inner circle.

Although several studies have focused on the artistic production of the Royal Family, analysing its historical context [4–6], style and iconography, the materials and techniques used for this ceramic production have not been investigated. In this study, we analysed a unique paint box by the maker Lacroix, Paris [2], with 31 tubes of ceramic paints (Figure 1A) detained by Palácio Nacional da Ajuda (PNA). Paint materials were analysed using x-ray diffraction (XRD) for mineralogical characterization, energy dispersive x-ray fluorescence (EDXRF) for elemental composition, scanning electron microscopy (SEM) for the observing of the microstructure and hyperspectral imaging (HIS) to identify the chromophore ions. For comparison purposes, a set of ceramic objects produced by Queen D. Maria Pia and King D. Fernando II belonging to the collections of PNA and of Fundação da Casa de Bragança (FCB) (Figure 1B and C) were also analysed using non-invasive methods (HSI and EDXRF).

A total of 31 ceramic colourants were analysed, where the main chromophore ions identified were

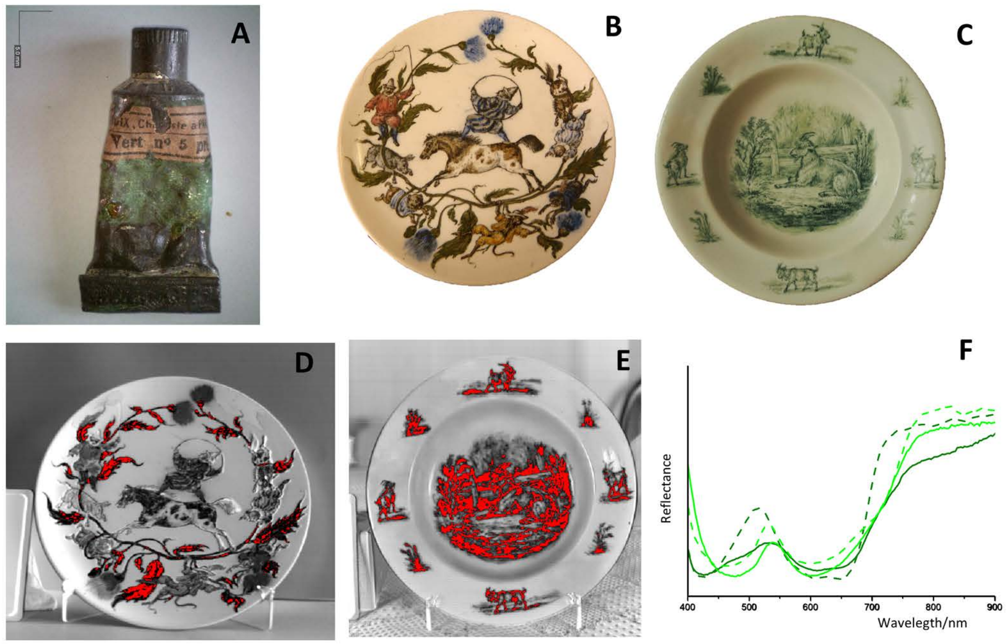

Figure 1. Example of a tube with ceramic paint (A). Ceramic plate painted by King D. Fernando II from PNA (B) and mapping of green colour HSI results (D); Ceramic plate painted by King D. Fernando II from FCB (C) and mapping of green colour HSI results (E); Reflectance spectra of two green paint materials (full) and of the painted ceramic objects (dots) (F).

Co for blues, Cr for greens (Figure 1D, E and F), Sb-Pb for yellows, Fe for browns and oranges, Cr, Co and Fe for black and greys, and Cr for pink. The elemental composition of the glaze applied over the ceramic objects showed the presence of Al, Si, K, Ca, Ba, Fe, Co, Cu and Pb, indicating the use of a lead silicate glaze. The ceramic objects were decorated with the underglaze technique, which involves applying the paint directly over the ceramic body. The colourants detected on the objects were similar to the ceramic colourants found on the paint tubes.

Acknowledgements

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The Portuguese *Tijomel* industrial complex

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SUMMARY: The 20th century post-war modernist architecture in Portugal renovated the tradition in the use of ceramic tile – azulejos – as an external coating material, either for protection or aesthetic purposes. The demanding for that manufactured product had always involved a specialized industry, which guaranteed the chain supply at a large scale, establishing important ceramic manufacturing centres. Nevertheless, at a regional level, numerous ceramic plants had also a significant relevance. This was the case with Júlio Redol's factory, 'Fábrica de Materiais Cerâmicos' located in Caxarias, which was founded in 1941 and ceased its activity in 1985. Later in 1961, rebranded 'Tijomel', has produced several construction materials such as ceramic tiles for coverings, ceramic bricks and precast ribs for lightweight concrete slabs. This paper focuses on 'Tijomel's' activity, mainly on the production of ceramic tiles – azulejos and pastilhas-, manufacturing techniques and applications, on local/regional modernist architecture building.

KEY-WORDS: Ceramic glazed tiles; Tijomel factory*; Portuguese Modernist Architecture; construction materials.*

INTRODUCTION

The Portuguese tradition of coloured tiles, azulejos, has persisted until today. In the 20th century, Modernist Architecture exploited this century-old tradition and achieved some innovation on its use in relation with industrial production, such as small and medium-sized semi-industrial units.

'Materiais para a Edificação, Lda.' was a Portuguese ceramic manufacturing factory founded in 1941 by Júlio Redol (1915-1992). In 1961, the factory was renamed 'Materiais Cerâmicos Tijomel' (*Tijomel*). Despite the local and national relevance of the factory and its ceramic products, there are very few written records on the production procedures.

The industrial facilities were located at Caxarias-Ourém nearby Júlio Redol's hometown, Tomar. The location was chosen because of the existence of clay deposits, and wood wastes to burn into the factory ovens.

In 1957, *Tijomel* employed 170 workers. By that time, the plant facilities had 26,000 m^2 in use, instead of the initial 4,000m^2 [1]. In addition to the different ceramic products, the plant manufactured kitchen furniture and precast concrete ribs and hollow ceramic bricks to assembly lightweight concrete slabs [2].

The *Tijomel* factory production units used different brands depending on the manufactured products, developing labels that were used as a brand name for each product.

Glazed ceramic tiles: the Decormel label

By the end of the 1950s, *Tijomel* launched a new product line - *Decormel* – intended for small

ceramic pieces, until then imported from Italy. *Decormel* was the label for decorative glazed ceramic tiles manufactured of red clay using the single-firing process, an innovative processing method [3] in the Portuguese ceramic industry at those days. These ceramic tiles were manufactured for the first time at *Tijomel* in 1957 [1]. Afterwards, the new ceramic product was presented in the national industry exhibition, 'Feira das Indústrias Portuguesas', where it had a good acceptance among architects and decorators. *Decormel* ceramic tiles were integrated in the Portuguese pavilion at the 1958 Brussels World's Fair, the first international exhibition after the Second World War.

Despite its valuable contribution to Portuguese modern Architecture [4, 5] the factory closed in 1981, after a period of financial crisis.

Methodology

While there's has been a growing interest referring not only to the interdependent relation between modernist architecture and the use of ceramic tiles [6,7] and plus the relevance of *Tijomel* role [5], the study of a regional industrial complex such as *Tijomel*, even if focused on a small part of its productive activity presents several difficulties, mainly due to the lack of information and property records.

So, this initial study was mainly based on the testimony of Júlio Redol's daughter, Mrs. Maria Helena Redol, and on a family book referred to the 10th anniversary of *Tijomel* [1], in 1961, credited to the Portuguese writer Alves Redol (1911-1969), Julio Redol's cousin. This book contains pictures and descriptions of the factory development stages [1]. The research on *Tijomel* factory and the dissemination and use of *Decormel* products in local modernist architecture was based on documentary research into institutional and private architectural records. The results of this research allowed to verify the interactions between architects, clients, and local industrial production.

This work, an extension of former research project about Modernist Architecture in Tomar [8, 9], intents to disclose the historical context of *Tijomel* factory and underline the influence of modernisation factors including industrial production methods, technological outputs, and innovative materials in modernist architecture. In this context, this study also intends to contribute to the rising of traditional and local techniques and procedures, when local resources and traditional architectural features were put in balance with modern values.

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Preserving artistic legacy: Cesare Brandi's restoration principles and Gestalt psychology in tile pattern panel conservation

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SUMMARY: The aim of the article is to present a specific tile restoration project conducted by the CAN-RAN atelier in a 19th-century building in Lisbon. The article explores exclusively the challenges faced by glazed tile pattern panels, particularly the issue of lacunae resulting from damage over the years. Drawing inspiration from Cesare Brandi's "Theory of Restoration", the article examines the guiding principles of restoration, emphasizing the importance of recognizing both the physical and aesthetic-historical dimensions of art.

In his work "Theory of Restoration," Cesare Brandi outlines various concepts essential for the restoration of artworks. He defines restoration as the recognition of both the physical and aesthetic-historical aspects of art, with the goal of passing it on to future generations. Restoration involves acknowledging the work's aesthetic and historical dimensions without erasing its aging signs. Brandi's Second Principle, which underscores the restoration of unity while steering clear of historical or artistic missteps, served as a guiding principle in the undertaking.

Central to Brandi's principles is the concept of organic-functional unity, stressing that perceiving missing parts as if contemplating a natural organism detracts from the genuine appreciation of the artwork. In this context, glazed tile pattern panels often confront the issue of lacunae, leading to an investigation into the principles of Gestaltism. The "law of enclosure" a foundation of Gestalt psychology, can play a pivotal role in addressing lacunae in glazed tile panels. By taking advantage of existing compositional elements, this psychological principle facilitated the completion of perceived gaps in the panels, allowing viewers to assume missing elements. Thus, the theoretical basis for the mental reconstruction of the missing parts of the restored tile panels emerged, perfectly integrating restoration concepts with the principles of Gestalt psychology. This synergy demonstrated the possibility of a holistic and conscious approach to the restoration process, enriching the theoretical basis for future efforts to preserve cultural and artistic heritage.

KEY-WORDS: Cesare Brandi, Gestalt psychology, organic-functional unity, glazed tiles, lacunae.

The organic-functional unity and Gestalt psychology

Restorers employ diverse methods to address lacunae in glazed tiles, with distinct approaches including pointillism, *trattegio* and volumetric reintegration[1]. An instance of volumetric reintegration involves the use of clay tiles to restore glazed tile panels exhibiting lacunae as in the example of the São João da Praça building, dating back to the early 19th century. Within its interior, there existed a glazed tile collection with numerous gaps in both patterned and ornamental coverings from the same period. The CAN-RAN atelier led the tile rehabilitation project with the objective of reinstating the unity of the diverse glazed tile panels. The approach aimed to accentuate the aesthetic value of the lacunae, allowing the new glazed tiles to evoke a previous state. The results are illustrated in the compositions below (Figure 1-3). In his work "Theory of Restoration", Cesare Brandi lists a series of concepts to be considered when restoring works of art. For Brandi, the definition of "restoration" is the *methodological moment of recognising the work of art, in its physical consistency and in its dual aesthetic and historical polarity, with a view to passing it on to the future*[2]. The Second Principle of Theory of Restoration arises from the balance between the aesthetic and historical instances: *restoration must aim to re-establish the potential unity of the work of art, as long as this is possible without committing an artistic or historical faux pas, and without erasing any sign of the work of art's passage through time.*[3]

Another fundamental aspect for understanding the whole work of art concerns figurative unity, as opposed to the organic-functional unity of existential reality, which resides in the logical functions of the intellect. This means that the image of the work of art is *truly and only what it appears to be*[4]. Brandi argues, for example, that a sculptural work of art in which only a hand or a head is represented does not mean that they are perceived as parts of an organism. The assumption of the other parts of this organism does not belong to the contemplation of the work of art, but rather to the regression of the work of art as a reproduction of a natural object.

Concerning the glazed tile coverings, the restored patterned glazed tile panel in São João da Praça can be viewed, in a theoretical context, as an organism. The acknowledgment of the remaining parts (lacunae) does not inherently pertain to the contemplation of the (new) representation of artwork. However, it is possible to go back, within the logical functions of the intellect, to the organic unity resembling a reproduction of a natural object – specifically, the original panel without lacunae. This is feasible perceptually through the ability to mentally "complete" the pattern in a logical exercise.

Figure 1. Composition: pattern with lacunae filled with clay tiles

Figure 1 shows a segment of a restored glazed tile panel, where the gaps have been filled using clay tiles. This panel features pattern tiles, evident in the repeated presence of the same motif. While the visual representation of the artwork is precisely what it appears to be, one can conjecture

that the original organic unity comprised the repetitive presence of the same motif in the absent sections. Similarly, when examining a patterned tile panel with gaps in the mouldings, one can assume the appearance of the absent tiles. Figure 2 is a good example:

Figure 2. Composition**:** moulding with lacunae filled with clay tiles

This logical exercise becomes feasible through one of the principles of Gestalt psychology: the law of enclosure[5]. This principle states that objects perceived as closed are considered complete, even if not entirely so. In the composition above, two distinct groups are enclosed resembling a discontinuous line due to its design. Consequently, perception "fills in" the missing pieces within this glazed tile panel.

An experimental study was carried out of the observers' assessment of the possibility of mentally recovering the pattern. It was found that in the compositions shown above, it was possible to mentally retrieve the original pattern. The disposition of the gaps has an influence on this mental exercise, but it is mainly the number of gaps that determines it. When there are a significant number of lacunae in a patterned tile panel, the perceptual reconstruction of the unit is not feasible. In this case, we are presented with the concept of "ruin", according to Brandi.[6]

The case study of *São João da Praça* serves as a compelling example, illustrating how the use of clay tiles in patterned panels allows the perception of the panels' organic unity. This is achieved through the law of enclosure, and, at the same time, respecting the principles outlined in Cesare Brandi's Theory of Restoration, although not complying with the restorations mentioned by the author, because of the emphasis of the lacunae in the new glazed tile panel.

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Assessing the thickness of ancient *azulejos* with GPR

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SUMMARY: The aim of "Layers" research project is to investigate the walls and floors of heritage buildings using geophysical methods to help understand their construction history and the evolution of their wall decoration with azulejos. In some cases, missing panels of azulejos may be hidden by recent layers and coatings and their discovery with non-destructive methods will be extremely important.

Glaze tiles at São Roque Church, in Lisbon, have an important and recognized heritage value. The panels were produced by several workshops, over a very long period since the 16th century.

Azulejo is a challenge to geophysical methods, in particular due to its low thickness. As thickness is higher for older azulejo, and São Roque Church present several azulejo panels from 16th to 19th centuries, some of them were surveyed with a Ground Penetrating Radar (GPR) equipped with a high frequency antenna (2.6 MHz) to evaluate its capability of identifying the interface between the back of the azulejos and the mortar, and the difference in the thickness of the tiles from the different production periods.

Here we present examples of the results obtained on four different productions of tiles from the 16th to the 20th centuries. They are used to illustrate the application of this non-destructive method to this particular material.

Another aim of this survey is to try to find the dielectric constant value associated with the ceramic body material. This information is considered relevant for the assessment of the thickness of ancient azulejos and as data that may be useful when dealing with similar cases.

KEY-WORDS: Ground Penetrating Radar; Glaze tile thickness; São Roque Church

Within the framework of "Layers" research project that aims to apply geophysical methods to the study of walls and floors of heritage buildings, a study is undergoing to evaluate the thickness of ancient *azulejos* from different production periods using a GPR equipped with a high frequency antenna (2.6 MHz). Previous tests [1] have already showed that the higher the antenna frequency

the better the results for such a thin target. One must state that GPR is usually applied to locate targets with contrasting dielectric properties from the surrounding environment, usually with decimetre to meter dimensions and located at depths up to about 8-10 meters. This shows the challenge that represents applying GPR to *azulejo* studies.

On Figure 1 is presented the radargram obtained in a profile, with a length of almost 1.60 m, performed over a 16th century panel. The top relatively uniform layer is interpreted as the *azulejo* body, with the interface between its back face and the mortar represented by the green reflector marked with a dashed black line, at a time-depth of about 0.40 ns. The reflections at greater depths are due to the wall material. At the beginning of the profile (on the left side of the radargram) the *azulejo/*mortar interface is not so visible, perhaps due to the strong reflector (in red) present just after the door, which may be related to the materials used to support the door frame, which cannot be as heterogeneous as in the rest of the wall.

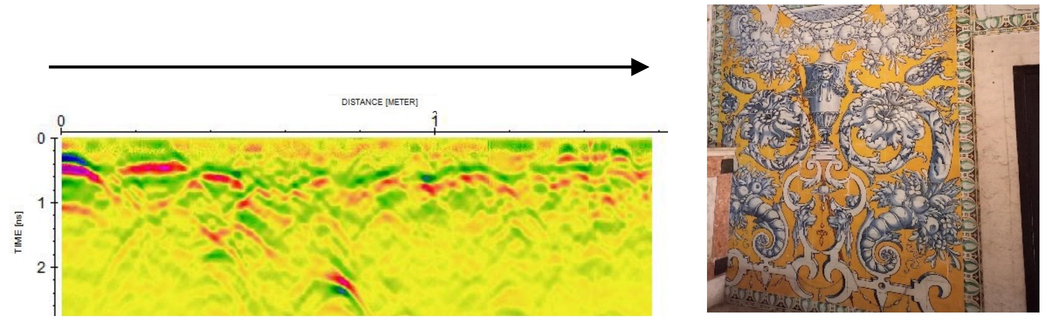


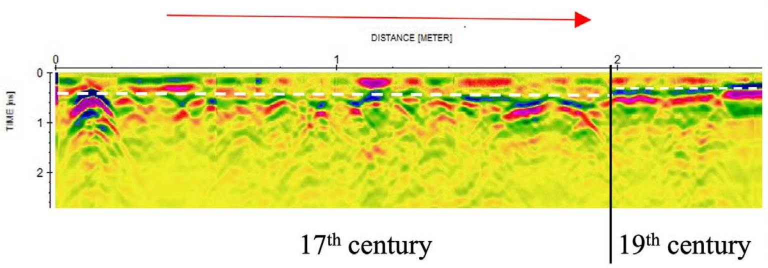
Figure 1. Radargram obtained in an *azulejo* panel from the 16th century (the black arrow shows he survey direction)

Figure 2 presents a second example, namely the results gathered over part of a wall covered by 17th century *azulejos*, from ground until about 2.0 m of the profile length, and, after that, a 19th century *azulejo* panel. As in the previous case, the interface *azulejo*/mortar is interpreted in the radargram as the green reflector marked by white dashed lines. The section from the 17th century presents a higher time-depth (about 0.40 ns) than the newer one (about 0.30-0.35 ns); these differences are an indication of the presence of tiles with different thicknesses. In fact, *Azulejo* samples from the same periods' present thicknesses of about 15-17 mm (17th century) and 10-12 mm (19th century).

Another feature that appears from this survey is a difference between the materials just below 19th century *azulejo* and those in the remaining section, since in this part there is a uniform, continuous and strong reflector (reddish). This is interpreted as a stronger and uniform mortar than the older one, present below the 17th century *azulejo*.

On the left side of the radargram, near the floor (survey beginning was at 0.28 cm above ground), a pattern that can be attributed to an old pipe is clearly visible centred at about 0.12 cm from the beginning of the profile (about 0.40 cm from ground).

Given the time-depths obtained and the corresponding *azulejo*'s thicknesses, the dielectric constant for *azulejos* may be estimated as comprised between 14.0 and 19.0.



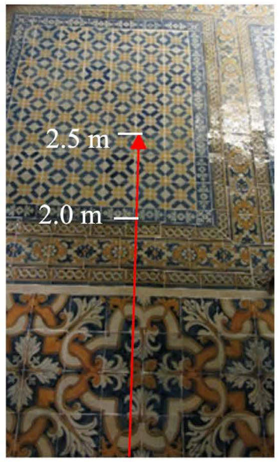


Figure 2. Radargram obtained in a wall covered with two azulejo panels, one produced in the 17th century (until about 2 m above ground) and, above, the second one, produced in the 19th century (the red arrow shows the survey direction)

For comparison, an example of modern *azulejos* (ca. 1970), obtained over a 5 mm *azulejo* panel installed on a concrete wall, is presented in Figure 3. In this case the *azulejo/*mortar interface is not clearly identifiable, which is attributed to the low thickness (low time-depth) when compared to the wavelength of the electromagnetic wave generated by the GPR antenna. The green and almost continuous reflector present at 1.0 ns time-depth is interpreted as the interface mortar/concrete (the hyperboles are reflections from the iron rebars).

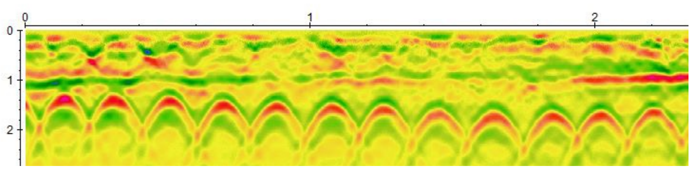


Figure 3. Radargram obtained in a wall covered with 20th century *azulejo*

Besides the difficulties and limitations of using the method for this purpose, the results obtained, and here illustrated, allow having a very positive perspective for the continuation of the work. These preliminary results show that the interface of ancient *azulejo*/mortar can be identified, and some features related with the homogeneity of the mortars used is also noticeable on ancient *azulejo* panels from which is expected that *azulejo* linings covered by a later render or by wood decorations may also be tentatively identifiable.

Acknowledgements

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The back of a tile and its alphanumeric codes: a case study of a group of 18th-century Portuguese azulejos

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SUMMARY: *During a conservation and restoration work in progress at the National Tile Museum, in Lisbon, several overlapping marks with different colours and inscriptions were identified on the back of the azulejos in an 18th-century blue-and-white panel.*

KEYWORDS: Panel; Azulejo; Coded marks; Alphanumeric codes

As part of a master's thesis in development, a study of conservation and restoration is being carried out on an 18th-century *azulejos* panel. This panel painted in blue and white, possibly represents a Roman emperor inscribed on suspended medallions (an unusual iconography for 18th-century *azulejos*). It is part of a set of four, which belong to *Museu Nacional do Azulejo* in Lisbon, and its provenance is unknown (Fig. 1 and 2). During the present study, several overlapping marks with different colours and inscriptions were identified on the back of the *azulejos*.

A comparison will also be made between panels one (Fig. 3 and 4) and two (Fig. 5 and 6) to find any logical connection between the marks.

Azulejos, the traditional glazed ceramic tiles commonly used in Portugal, often contain coded marks that help identify their location and positioning on each panel. These marks may also provide insights into the production methodologies. The system emerged from the need to establish a connection between the *azulejos* and architecture and is based on alphanumeric marks, which emerged over time to facilitate the placement of *azulejos* in their desired position on the panel, as the figurative order became more complex. The alphanumeric marks consist of three essential elements: letters indicating the vertical position, numbers identifying the horizontal position, and another symbol that identifies the belonging of the *azulejo* to a particular panel [1, 2 e 3].

After a preliminary examination, it has been observed that the panel contains a maximum of three overlapping marks. Each mark has a different colour and handwriting, suggesting that they were made at different periods and by different individuals. The first mark is black and strongly adhered to the ceramic, which could indicate that it is the original one. The second mark is also black (less adhered than the previous one) and the third is blue (the most recent one because it is above all the previous marks) - both are relatively superficial and easily removable with water.

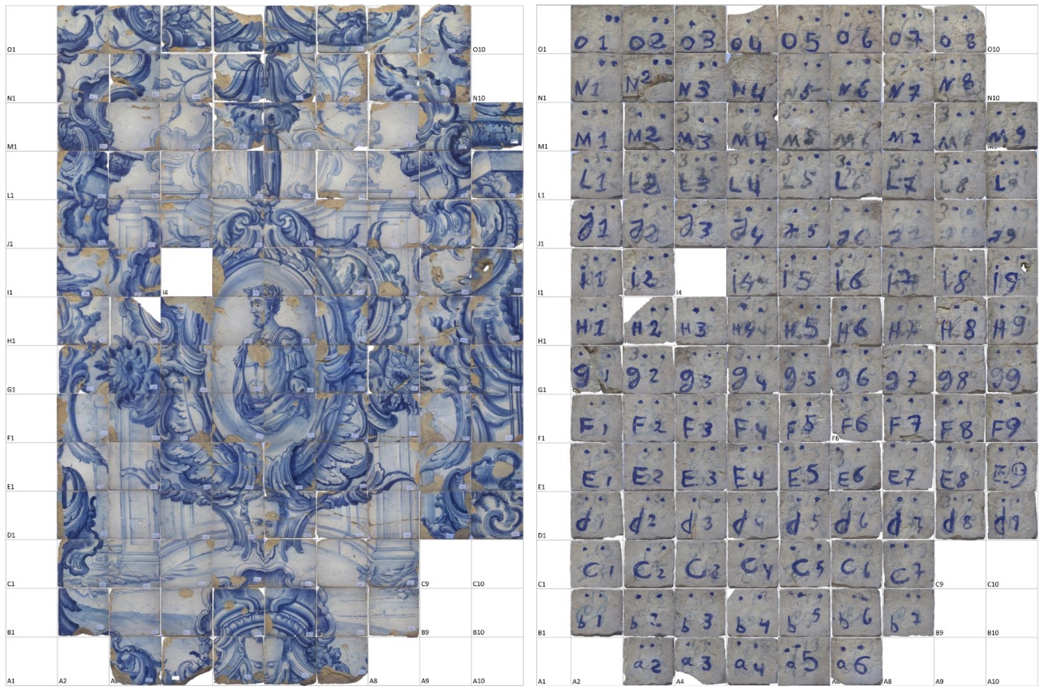

Figure 1 and 2. Panel 1 (image front and back). Author: Margarida Martins

To complement the study of these multiple marks, material characterization of the paints used will be carried out by XRF (X-ray fluorescence) analysis, to provide elementary information, identify the composition of the paints and, if possible, associate it with a specific period of use.

It is known that few studies have been dedicated to back marks, because of the major importance of the vitreous layer. However, it is important to invest in studying these marks to understand the history of these panels and why different overlapping marks were used.

The *Museu Nacional do Azulejo* continues to conduct in-depth research on these elements and aims to provide more insights in the near future [1].

Figure 3 e 4. Panel 1. (image front and back of azulejo).
Photoshop edit. Author: Margarida Martins

Figure 5 e 6. Panel 2. (image front and back of azulejo).
Photoshop edit. Author: Margarida Martins

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Specific glaze colour degradation in Portuguese 17th-century tiles

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SUMMARY: Throughout several years of practical work on the conservation and restoration of Azulejos, as in frequent discussions with colleagues related to different approaches to Azulejos, the degradation of glazing associated with colour has been a constant theme. Its evidence is flagrant, and although empirical knowledge allows us to understand this behaviour, the phenomenon of this degradation has never been studied, consequently, its minimization procedures have not been developed, and the Azulejos heritage continues in a process of loss.

KEY-WORDS: Azulejos, Detachment of glazes, Glaze colour behaviour

Glaze detachment is the more obvious form of decay in ceramic tiles because it leads to the loss of the pictorial content and, consequently, of all the aesthetic significance of these artistic objects. There are several factors for the decay of the glazed surface in tiles, being the starting point the presence of water/moisture that makes soluble salts a problem and contributes for the proliferation of biological contamination, both decay factors by the irreversible expansion of the ceramic and spontaneous fissuring.

Manufacturing defects should obviously be considered, but there is not an explanation for its association with the degradation related to specific glaze colours. Tiles with manufacturing defects may have their glaze partially cracked or delaminated, thus offering easy routes for moisture propagation, biological contamination, salt crystallization and decay. Salt crystallisation causes and spreads fissures and intensifies the porosity of the glazed surface due to its deterioration, as the porosity of the biscuit, increasing the circulation of water in it. Moisture contributes to biological growth, chemical reactions, lixiviation, and freeze/thaw physical damages.

However, even understanding the different causes of this degradation process, which are usually related to each other, it's difficult to understand how the same tile can show different degradation behaviours related to its colours under the same conditions. (Figures 1 and 2).

Figure 1 and 2: Examples of glaze detachment specific to the white glaze.

This case study aims to compare the different behaviours observed on the blue and white glaze applied in tiles exposed to the same environmental conditions (Figures 1 and 2). These tiles, dated from the 17th century, belonged to *Convento de Santa Clara*, in Funchal (Madeira, Portugal) (Figure 3). They are decorated in blue and white in a pattern known as "Falsos Enxaquetados".

Figures 3 and 4: Convent of Santa Clara, in Madeira, and the original location of the tiles

The analytical study in development is based on observations by optical microscopy (OM), X-ray fluorescence spectroscopy (XRF) and analytical characterisation by scanning electron microscopy (SEM). Through OM and SEM, manufacture defects, cracks and fissures causing glaze detachment from the biscuit can be identified for each colour, helping us to understand the different behaviour between the blue and white glaze. From XRF, its possible to understand the composition of glazes and clay used in this Azulejos production.

The case study presented here is part of the ongoing PhD research project "*A journey through colour in Portuguese tiles between the 16th and the 18th centuries. Technology and restoration*" included in the project ChromAz (PTDC/HAR-HIS/1899/2020) and focusing on the study of colour and the degradation processes associated with it.

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Study of the tiles of Plaza de España (Seville, Spain). A model for characterization and preventive conservation

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SUMMARY: The presented research aims to study of the ceramic materials of Plaza de España to develop a long-term model for preventive conservation. Specific objectives include a) understanding the types of raw materials used and their origins, b) assessing the firing temperature of ceramic pieces and manufacturing processes, c) comparing the original pieces with those currently on display to identify any potential deterioration, and d) proposing improvements for restoration/conservation.

KEY-WORDS: Ceramic materials, Mineralogy, Characterization, Plaza de España, Tiles

INTRODUCTION AND OBJECTIVES

Plaza de España in Seville, Spain, stands as an unique monumental ensemble within the regionalist architectural style, showcasing how Sevillian tiles can adorn one of the city's most emblematic landmarks. Constructed with exposed brick and adorned with ceramics, wooden ceilings, carved marble, wrought iron, and embossing, this square is of significant interest, particularly the tile benches that depicted all the provinces of the country during its construction for the 1929 Universal Exhibition in Seville[7]. Some original pieces were not exposed, and they are currently stored in the premises of the Special Delegation for Economy and Finance of Andalusia. The remaining tiles have been gradually restored based on the environmental or human deterioration they have experienced in recent years[8,9].

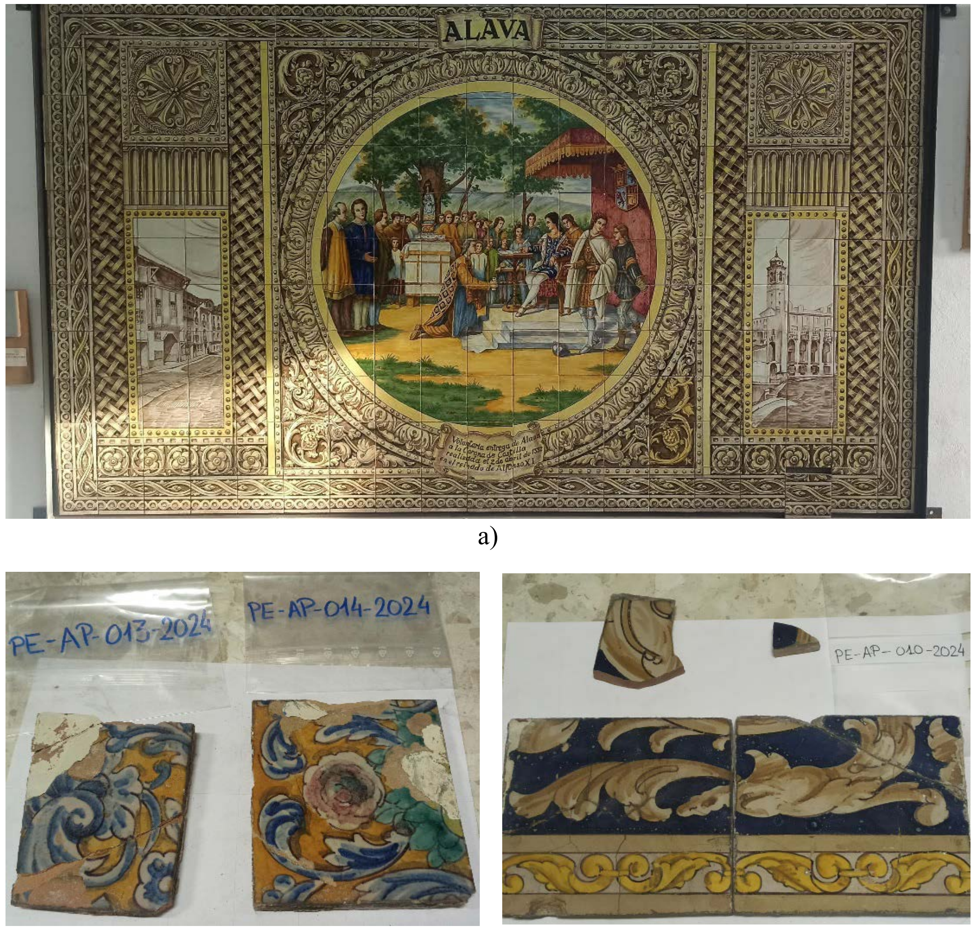
In the initial stage of the research, the focus has been on the systematic study of ceramic pieces (tiles), aiming to reveal the origin of the materials used. Given the historical and artistic value of these ceramics, their study may be constrained by the need to preserve the integrity of each piece. This implies the use of non-destructive techniques or those causing minimal impact on the fragments and the displayed tiles.

MATERIALS AND METHODS

The selection of appropriate raw materials to produce clays, which will later be fired, is crucial in achieving the desired quality in ceramic pieces (moderate shrinkage during drying, suitable porosity for glaze adhesion, flexural strength, etc.). Manufacturing methods and procedures also play a fundamental role in determining the characteristics of the final piece. Therefore, mineralogical and chemical characterization of both original and currently displayed samples from the benches of different provinces in Plaza de España has been conducted. All described analysis were developed at the General Research Services of Seville University (CITIUS).

- Original Tile Samples

A total of 26 samples (Figure 1) were collected from original tile panels on the benches representing various Spanish provinces (Avila, Salamanca, Logroño, Zaragoza, etc.), covering different years of manufacture between 1920 and 1926.



a) b) c)

Figure 1. Original tiles from Plaza de España. **a)** Panel representing the surrender of Alava to the Crown of Castile during the reign of Alfonso XI, **b)** samples of the bench under Guadalajara panel, **c)** samples of the bench under A Coruña panel.

The following analyses were performed on each sample:

Mineralogical Characterization: Utilizing X-ray diffraction (XRD), the total sample analysis was conducted using the powder method (random powder orientation). Selected samples underwent scanning electron microscopy (SEM) for texture analysis and chemical composition using backscattered electron imaging with an energy-dispersive X-ray detector (EDX).

Chemical Characterization: The chemical composition of the samples was determined through X-ray fluorescence. For samples with insufficient quantity, the chemical composition was determined using micro-X-ray fluorescence with the EDAX Eagle III equipment. Thin sections were prepared from selected samples for further examination using a polarizing Zeiss Junior microscope with an external Nikon CoolPix 4500 camera.

- Samples Currently on Display

Given the logical constraint that these samples cannot be broken for characterization, the analyses have been carried out using non-destructive methods.

- Glazed Materials

For the comprehensive chemical analysis of glazed ceramic surfaces, micro-X-ray fluorescence (μXRF) was employed using an EDAX Eagle III machine. The equipment is equipped with Rh Kα radiation and an EDAX detector. This methodology enables non-destructive chemical analyses of the ceramic objects' surfaces, along with elemental 2D mapping. The surface analysis provides valuable insights into the composition and distribution of elements in the glazed ceramic materials.

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Co-creating scientific knowledge towards the technological memory of the glazed ceramics production

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SUMMARY: This reflection discusses and deepens the methodological paths of construction and innovation of scientific knowledge on the memory of the technological processes of production of glazed ceramics, their materials, ways of doing and know-how dynamics. To this end, it addresses the notion of co-production of scientific knowledge related to the study of these memories. The aim is to discuss the contributions with/using a dialogic perspective between social sciences/ anthropology, history/art history, conservation/ restoration, natural and exact sciences, and digital technologies. More specifically, the synergetic dynamics between a historical and anthropological perspective of the construction of knowledge, in which the use of qualitative methodological approaches and devices predominates, and a technical-scientific, experimental and laboratory approach to the production of scientific knowledge, also highlighting the potentialities that digital technologies can have in increasing this purpose. In the development of the work, we use specialized literature and provide examples, where we examine studies based on research projects, observing achievements, challenges, and opportunities of co-creating scientific knowledge.

KEY-WORDS: Glazed ceramics; Technology; Production know-how; Interdisciplinarity.

CO-PRODUCING SCIENTIFIC KNOWLEDGE

In a previous work, the importance of studying glazed ceramics, namely tiles, was defended with the aim to value the not so visible aspects of its industrial production – the materials, the technical processes used and the underlying production know-how [1]. Towards the same purpose, it was considered of interest to deepen the scientific knowledge from three articulated lines of investigation: historical, material characterization and replication, and the collection of oral narratives around the themes of the memory of technological production. For the present reflection, this tripartite perspective of the study of glazed ceramics, in general, and tiles, in particular, is taken up and deepened, considering the dialogical contribution between social sciences/anthropology, history/art history, conservation/restoration, natural sciences, exact sciences and digital technologies applied to the study of cultural heritage (Figure 1).

This reflection focuses therefore on the advantages of adopting a co-production perspective of scientific knowledge creation, evoking the role of interdisciplinarity, more than just the multidisciplinary interaction. It is assumed that the value (or even values) of glazed ceramics, in particular tiles, is (also) related to their production technique. For the study of this production-

technological memory, it is therefore considered important to stimulate the interaction between different disciplinary fields/sciences in and for the construction of scientific knowledge. With the aim to highlight the impact of using this common effort, real examples of the performed work are provided. From an anthropological approach, it focuses on the contribution that qualitative methodologies have in the deepening of scientific knowledge about materials, production processes, creation, application, and correspondent technological knowledge involved – and which are not necessarily scientific. It is demonstrated how this effort has contributed to reconstruct part of the intangible heritage associated with such ceramic materials – production techniques, knowledge, tools, materials – also highlighting related socio-cultural aspects. It is evidenced the contribution of history/art history to contextualize moments and formulate hypotheses that will help natural/exact and conservation scientists to break new grounds/blazing trails for obtaining scientific knowledge, namely from the study of the materials and its relationship with technical (non-scientific) production know-how.

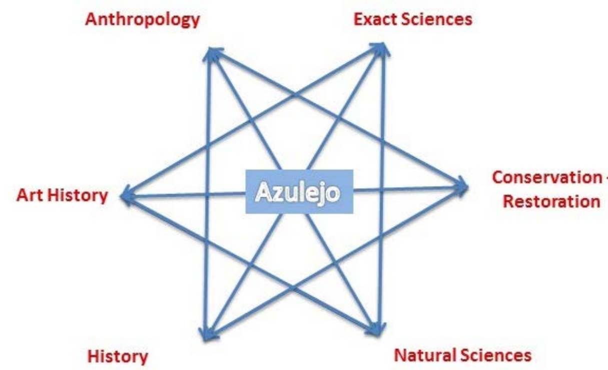

Figure 1. Co-producing scientific knowledge.

Along with the potentialities and achievements of co-production, some of the challenges and opportunities of knowledge are also discussed, reflection to be even more instigated having in consideration the novel resources brought by digital technologies. The heritage – tangible and intangible – related to the industrial production of glazed ceramics in Portugal, is the historical, geographical and cultural context of reference. Where, despite the general recognition of the importance of technological processes in the studies of ceramic heritage, and the many advances in this field of knowledge in recent years, much remains still to be known, along with the imminent vulnerability of this material and immaterial heritage. Gaps in scientific knowledge about the origin of material components, compositions, procedures, techniques and solutions used are still existent, together with a lack of documentation, since much of this technical knowledge has been obtained and transmitted, generally, verbally and by observation.

For the development of the present work, we resort to specialized literature (historical, methodological, sociocultural, from exact and natural sciences, conservation and restoration, etc.), and to studies based on research projects in which the authors participated. Examples are highlighted for instance where the subject of study has been instigated by history/art history, exact/natural sciences, conservation/restoration or social/anthropological questions, and the methods to address those issues also involved those disciplines.

This synergetic interdisciplinarity was observed during the collection and analysis of the materials to study (through laboratory studies, *in situ* observation), historical and documental research, oral narratives (through interviews), imagery and audiovisual (through observation and recording in *situ*, consultation in physical and online archives). This reflection aims therefore to highlight the potential of co-production of scientific knowledge, also emphasizing and valuing the heritage underlying the technological memory associated with the production of glazed ceramics.

Acknowledgment

This work was developed within the scope of the following research projects and programs: 1) P2I Ceramic – Study and Conservation of ceramic materials; 2) Research Program Integrated Methods for the Conservation and Rehabilitation of Built Heritage – MICR of the Research and Innovation Strategy (E2I) of LNEC 2021-2027. Fundação para a Ciência e Tecnologia is acknowledged for the financing of "Old azulejos through new lenses" project (DOI 10.54499/2021.01998. CEECIND/CP1703/CT0001).

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Challenges in developing a qualitative approach on the perception of tiles decay

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SUMMARY: Among the objectives of the "Old azulejos through new lenses" and "P2I Ceramic" projects, is the aim to understand the perception and information that owners, managers and/or other relevant personalities have about the probable causes of the deterioration of tile panels. That is, how the responsible for the objects perceive the probable causes of the tiles deterioration. On the other hand, they aim to obtain information about the importance that these interlocutors attribute to the tiles under their tutelage or supervision and to the need to adopt preventive conservation and restoration actions to protect them. This instigated the establishment of a dialogue between the sciences that have traditionally studied the deterioration and conservation-restoration of tiles (exact sciences, construction industry, conservation sciences) and the social sciences. The purpose of this work is, from the perspective of the social sciences, to highlight the potential of this interdisciplinary perspective for the study of tile deterioration. In addition to the challenges that arise, the objective is also to highlight the contribution that a qualitative approach to the study can have to the process of construction and innovation of scientific knowledge, considering, in parallel, the contribution to the field of conservation and restoration of tiles heritage.

KEY-WORDS: Tile decay; Conservation; Safeguarding; Heritage; Memory; Meaning and value.

Focusing on studying historic tiles to contribute to their safeguarding, the "Old azulejos through new lenses" and "P2I Ceramic" projects aim to develop methodologies for collecting, acquiring and recording information (history, constitution and state of conservation), for the analysis and monitoring of the deterioration state of tiles that will enable more effective, efficient and conscious action of their safeguard. However, all the possible causes that provoke the deterioration of these tiles cannot, or can be easily, captured through technical and scientific studies, because certain contextual conditions of the use and architectural environments where these tiles are inserted may have also played a role in their deterioration.

One of the objectives of the projects is to investigate these aspects based on the perception that owners, managers and/or similar personalities make of the probable causes of deterioration of tiles. That is, it is intended to capture how these interlocutors perceive [1] the conditions of construction, use and maintenance of the spaces in which these tiles are located, the knowledge of previous occurrences (such as flooding and water infiltrations) and to identify what they point out as likely contributions to deterioration (Figures 1 – 3).

However, it is also important to better understand the importance (meaning and values) that these interlocutors attribute to the tiles under study, because this aspect also interferes with the extent of care that is or can be taken by preventive conservation and the possibility and type of restoration interventions that could be considered. In order to fulfill this purpose, it is planned to question the respective interlocutors using a qualitative approach. This methodological strategy points out the potential contribution of the Social Sciences to the construction and innovation of scientific knowledge, by adding a more dialoguing and interdisciplinary approach and action perspective in the field of conservation and restoration of tile heritage.

Figure 1. Lack of maintenance, loss of tiles and unappropriated interventions.

Figure 2. Effect of decay. Glaze lacunae at the edges of the tiles.

Through the development of open and semi-structured interviews on specific topics, information will be obtained that will then be object of content analysis, with respective systematization and hierarchical categorization. At the same time, this survey procedure will be integrated by a short questionnaire that will include an evaluation scale on the importance and meaning of the tiles as assigned by the interviewees, as well as an evaluation and hierarchy of the probable causes of deterioration based on the perception and knowledge of the situation by the referred participants.

Figure 2. Lack of maintenance, loss of tiles and unappropriated interventions.

It is expected that the knowledge obtained, in addition to being integrated into the broader set of results of the “Old azulejos through new lenses” and “P2I Ceramic” projects, will also contribute to raise awareness and empower the project team and related professionals for the potential resources of qualitative methodologies and, as such, of the Social Sciences, for the conservation and restoration of tiles heritage. At the same time, it is foreseen that the knowledge obtained may contribute to the achievement of a broader purpose of science communication to raise awareness for the conservation and safeguarding of the historic tiles to the specific (e.g. owners, managers and/or similar personalities) and general audiences.

Acknowledgment

This work was developed within the scope of the following research projects and programs: 1) P2I Ceramic – Study and Conservation of ceramic materials; 2) Research Program Integrated Methods for the Conservation and Rehabilitation of Built Heritage – MICR of the Research and Innovation Strategy (E2I) of LNEC 2021-2027. Fundação para a Ciência e Tecnologia is acknowledged for the financing of “Old azulejos through new lenses” project (DOI 10.54499/2021.01998. CEECIND/CP1703/CT0001).

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Theoretical-methodological challenges to the study and safeguarding of industrial tile production memories. The case of the Constância Ceramics Factory in Lisbon

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SUMMARY: This work addresses the field of memory related to the industrial production of ceramics in Portugal between the 19th and the 20th century, namely the knowledge of materials and techniques of tile production. The study of the industrial and socio-technical memory is seen a way to enrich technical and scientific knowledge and, thus, contributes to enable more conscious practices of conservation and restoration of the tile heritage, alongside to the safeguarding of this same memory. With this objective, the theoretical and methodological perspective of the research (which is under development) is performed over the case study, of the memories of the socio-technical aspects, of the Fábrica de Cerâmica Constância (Constância Ceramic Factory), in Lisbon.

KEY-WORDS: Tile factory production, Industrial memory, Technical knowledge, Tile heritage conservation

In the field of conservation, restoration and safeguarding of cultural heritage it is crucial to consider the relationship between materiality and immateriality [1]. The study of memory, having in view its recovery and safeguarding, echoes this motto by resurfacing certain social facts, objects, materials, knowledge and values, reframing and dignifying the past. It also allows the continuity of that memory into the future (and its transformations) and, as such, of the cultural heritage with which it is associated.

In the case of industrial tile production in Portugal between the 19th and 20th centuries, studies of history and respective industrial memory have been documented [2, 3, 4 and 5]. However, much remains to be researched, especially considering aspects related to the materials, procedures, and technical knowledge of the tiles production [6]. Given this situation, researchers from the National Azulejo (Tile) Museum (MNAz) and *Laboratório Nacional de Engenharia Civil* (LNEC) have, in a collaborative way and for several years now, tried to contribute to filling-up this gap in knowledge.

The *Fábrica de Cerâmica Constância* (Ceramic Factory Constância) -Figure 1, located close to the National Museum of Ancient Art, operated between 1836 and 2001. Since its foundation, this

factory has manufactured decorative and utilitarian ceramics. However, it is difficult to specify the date when the tile production began. Nevertheless, from the first years of the 20th century, this factory structure would come to stand out in the production of important references in Portuguese tiles history, as well as attracting renowned artists [7, 8, 9, 10 and 11]. In 2001 the factory activity was closed due to bankruptcy, and its assets sold a few years later. Around 2018, the factory buildings were to be demolished, leaving the equipment, documents, products and work materials found in the factory structure at risk of being lost (Figure 2). Therefore, also an imminent risk of loss of invaluable socio-technical memory.

Figure 1. Constância Ceramic factory. Left: factory logo; Middle: entrance to the factory facilities/shop before demolition; Right: after the demolition (Image by Pinto Soares)

Figure 2. Products and work materials left in the factory and found after its closure.

A team from MNAz and LNEC visited the site during the weeks before demolition to try and safeguard distinct aspects related to of the memory of the factory, a laborious and challenging activity. A PhD will be developed about this factory and its production which, hopefully, will build over the information and materials collected towards that purpose. The work will essentially focus on the study of sociotechnical memory [10 and 11]. To this aim, the following aspects will be addressed:

- the importance of studying industrial memory related to the ceramic production sector, specifically related to azulejo tiles, to understand and safeguard heritage also contributing to the implementation of more conscious tile conservation and restoration procedures;
- an overview of the history of the Constância Ceramic Factory and its role in Portuguese tile production;
- the risk of memory loss related to the Factory: bankruptcy, deactivation and destruction of the building, kiln and other assets, dispersion of former workers and their often-old age;

- the importance of collecting and analysing documental information, from image sources (photos and audio-visuals) and plans, maps and drawings related to the production process;
- the study of the productions, techniques, materials and artistic knowledge related to the tile production of this factory based on the material evidence and oral testimonies.

The points above will be documented to highlight the theoretical-methodological path that has been followed, also indicating the challenges that, from this perspective, arise for the survey, analysis and production of scientific knowledge.

Acknowledgments

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Geopolymers for glazed tiles lacunae in conservation practice

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SUMMARY: Glazed tiles are a definite mark in Portuguese architecture. Their thorough use in buildings from the 19th Century implies the actual need for conservation actions. Geopolymers are inorganic materials with a high application potential and their use was tested for filling "biscuit" lacunae. Results were promising but implied the need for further development of geopolymers suited for this specific use.

KEY-WORDS: Glazed tiles; Lacunae; Geopolymers

Glazed tiles (azulejos), are an important asset for Portugal, as they are relevant items in architectural history and a definite mark of the country's cultural past [1]. These tiles, commonly used as façade finishing elements, stand out because of their size and very particular aesthetics. Distinct production techniques used throughout their chronology [2], [3], affect how they respond to the actions of water, wear, and damage. Glazed tiles consist of a ceramic body called "biscuit" and a glazed surface [4]. The raw-materials and production techniques of the ceramic body are crucial in determining the tile's qualities. There are very relevant differences in tile properties throughout the ages is this is especially clear when comparing currently manufactured tiles and tiles used up to the beginning of the 20th Century. These differences arise from variations in the raw materials, the porous structure, and the effects of damaging factors, such as weathering, salts and exposure to chemical substances [4]. Applied tiles often display degradation patterns and need careful repair in order to maintain the overall characteristics of the façades. Lacunae are frequent and this kind of damage needs specific intervention so as to enable these tiles to be reused on the same surface.

The use of geopolymers has a long history, but their application in this context is relatively novel [5, 6].These are inorganic materials which possess a mineral origin, and their composition involves the use of a precursor, an alkaline activator and a solvent. The process of geopolymerization takes place by a chemical reaction that usually occurs in an alkaline medium, resulting in the formation of inorganic polymers with silicon and aluminum (connected by oxygen ions) as main constituents. The alkalinity of the solution is achieved through the use of activators such as sodium and potassium hydroxides and/or silicates. Geopolymers formed in this way have a varied composition and, henceforth, an array of characteristics when it comes to physical, chemical and mechanical performance [7].

It was considered relevant to test the use of geopolymeric materials as a possibility for the filling of missing tile fragments due to the fact that they harden without need for heating and also because of their inorganic matrix. The lack of heating needs enables a simple intervention for lacunae filling, whilst the inorganic matrix may be a plus in terms of durability, but especially in terms of compatibility with the ceramic tile.

The geopolymers used for this study were produced using metakaolin and different proportions of zeolite or fly ash and adding sodium hydroxide and/or calcium hydroxide as alkaline activators [8].

Geopolymer development presented difficulties in the first stages, generating cracking, retraction and showing the presence of salts after exposure. Therefore, it was necessary to improve the material, adjusting quantities and pH until a sample displayed no cracking, retraction or salts, after exposure.

Testing procedures involved the evaluation of geopolymer properties through water absorption by capillary action, accelerated artificial ageing and the determination of compressive strength.

It was found that the best performing geopolymer sample in terms of cracking performance showed the lowest mechanical strength and a high capillary absorption coefficient. Compressive strength values displayed a high variation at 28 days, ranging from 0,33 to 4,55MPa. Despite the possibility of using materials with low compressive strength, water absorption is critical and shouldn't be excessive. It is well known that ceramic samples have a wide range of capillarity characteristics, due to distinct raw materials, different production methods and varied exposure. However, it must be taken care that absorption of compatible materials isn´t excessive so as not to compromise the supporting walls, in cases in which a whole fragment is replaced by geopolymer.

Taking into account the experience performed with geopolymers as possible materials for the filling of lacunae in glazed tiles, some first steps were performed, both in terms of formulation and testing of properties. Although this is a potential material for use in conservation practice, a few steps must still be undertaken to ensure adequate compatibility and durability of a proposed solution that may be of current use.

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