LABORATÓRIO NACIONAL
DE ENGENHARIA CIVIL

A RESEARCH ON MANUFACTURING DEFECTS AND DECAY BY GLAZE LOSS IN HISTORICAL PORTUGUESE AZULEJOS

RELATÓRIO 24/**2011 – NPC/NMM**

LABORATÓRIO NACIONAL
DE ENGENHARIA CIVIL

DEPARTAMENTO DE MATERIAIS
Núcleo de Materiais Pétreos e Cerâmicos
Núcleo de Materiais Metálicos

Proc. 0205/11/17684
Proc. 0204/11/17692

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Plano de Investigação Programada do LNEC

Lisboa • Janeiro de 2011

I&D MATERIAIS

RELATÓRIO 24/**2011 – NPC/NMM**

A RESEARCH ON MANUFACTURING DEFECTS AND DECAY BY GLAZE LOSS IN PORTUGUESE AZULEJOS

SYNOPSIS

Portuguese glazed ceramic tiles- azulejos- are a distinctive mark of Portuguese culture. However they suffer from several pathologies that result in the loss of the glaze and, with it, of the pictorial layer. The few sources available about azulejo decay consistently point to the crystallization of soluble salts as a major cause of glaze detachments. But a review of azulejo pathologies throughout Portugal has shown that, although the presence of water is always associated with decay by glaze detachment, water is merely an aggent that may, or may not, result in widespread decay. Observations lead us to hypothesize a correlation between forms of decay usually associated with the crystallization of soluble salts and manufacturing defects. A supposition advanced for future verification was that, when challenged by aggressive conditions, azulejos without defects could remain macroscopically impervious while contiguous tiles with even minor defects of certain kinds would progressively suffer extensive glaze loss. That condition could arise even when the influence of soluble salts was seemingly negligible. Hence the importance of a clear understanding of the cracking patterns and other defects and how they influence decay.

INVESTIGAÇÃO SOBRE DEFEITOS DE FABRICO E DEGRADAÇÃO FÍSICA EM AZULEJOS HISTÓRICOS PORTUGUESES

RESUMO

Os azulejos constituem um traço distintivo da cultura portuguesa, mas estão sujeitos a diversas patologias de que resulta a queda do vidrado e, com ele, da camada pictórica. As poucas fontes existentes referem a cristalização de sais solúveis como causa primordial desses processos. Mas um conjunto de inspecções realizadas em Portugal mostrou que, embora a presença de água seja um traço comum aos processos de degradação, a água constitui apenas um agente que pode, ou não, causar um dano rápido. As observações realizadas conduziram-nos a reconhecer uma correlação entre alguns defeitos de fabrico e muitas das formas de degradação atribuídas exclusivamente à presença de sais solúveis. Segundo a hipótese então formulada, os azulejos sem defeitos poderiam manter-se macroscopicamente indemnes, enquanto que azulejos aparentemente idênticos com pequenos defeitos de determinados tipos, alguns dos quais invisíveis à observação, podiam, quando sujeitos às mesmas condições, sofrer processos rápidos de alteração e perda do vidrado mesmo quando a presença de sais parece diminuta. Donde a importância de estudar os defeitos de fabrico e a maneira como influenciam a degradação. É esse o tema central da investigação relatada neste Relatório.

A RESEARCH ON MANUFACTURING DEFECTS AND DECAY BY GLAZE LOSS IN PORTUGUESE AZULEJOS

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A RESEARCH ON MANUFACTURING DEFECTS AND DECAY BY GLAZE LOSS IN PORTUGUESE AZULEJOS

FIGURE INDEX

A RESEARCH ON MANUFACTURING DEFECTS AND DECAY BY GLAZE LOSS IN PORTUGUESE AZULEJOS

1- AN INTRODUCTION TO THE THEME

Figure 1 - Azulejos are a distinctive mark of Portuguese culture (Igreja do Terço, Barcelos)

Portuguese glazed ceramic tiles - azulejos - are a distinctive mark of Portuguese culture (figure 1). The conservation of the Baroque churches, palaces and even gardens calls for the conservation of the azulejo panels that decorate them. However they suffer from several pathologies that result in the loss of the glaze and, with it, of the pictorial layer (figure 2).

The available literature about decay of historic azulejos [1,2,3] consistently points to the crystalization of soluble salts as a major cause of glaze detachment. But a review of azulejo pathologies throughout Portugal [5] has shown that although the presence of water is always associated with decay by glaze detachment, water is merely an aggent that may, or may not result in widespread decay.

Figure 2 - Azulejos suffer from pathologies resulting in the loss of glaze
(Igreja do antigo Mosteiro de Jesus, Setúbal- December 2008)

On some historical sites the lower part of tiled walls suffers the effects of moisture with soluble salts present. However, the tiles are not affected and the crystallization, when present, occurs above the panel or, sometimes, behind the tiles without any loss of glaze. In many other locations, however, salt crystallization results in the blistering of the glaze and/or appalling loss of the pictorial layer, as in Palácio do Raio in Braga (figure 3). Such different behaviour could be dispelled through an explanation based on varying humidification conditions that in some cases cause crystallization in risky places, while in other cases the crystallization will naturally occur in harmless locations. However, one is often confronted with historic tiles from the same panel, some of which are strongly decayed while others that side with them seem almost immune (e.g. some of the tiles on the right side of the panel in figure 2 and some of the tiles seen in figure 3). The fact that some azulejo tiles or panels decay while others, seemingly similarly challenged, do not, lead to the conclusion that there must be some characteristics of tiles, either intrinsic or acquired, that make some of them more prone to decay. That conclusion was reinforced by the mentioned occurrence of varying degrees of decay within the contemporaneous tiles that make up a single panel.

Figure 3- Loss of glaze in a stairs hunt scene of the second half of the 18th century (Palácio do Raio, Braga - February 2009)

As for intrinsic characteristics, observations lead us to hypothesize a correlation between forms of decay usually associated with the crystallization of soluble salts and manufacturing defects. A supposition advanced for future verification was that, when challenged by aggressive conditions, azulejos without defects could remain macroscopically impervious while contiguous tiles with even minor defects of certain kinds would progressively suffer extensive glaze loss [4]. That condition could arise even when the influence of soluble salts was seemingly negligible. Hence the importance of a clear understanding of the cracking patterns and other defects that is the main theme of the present research report.

As for acquired characteristics, observations also lead us to suspect that a physical damage, as for instance the breakage resulting from an impact or the insertion of a nail, could soften a spot from where decay would progress that would not have occurred otherwise. We call this “the first damage hypothesis” and it explains why often tiles decay from the edges by twos, threes and fours, as in figure 3. In this particular case, a first damage could result from the interference between tiles caused by hydric expansion. The propagation of decay from a damaged area is being studied presently and will be the subject of a future publication.

2- METHOD

During 2009-2010 inspection visits were made to a number of monuments and sites with relevant sets of 17th and 18th centuries azulejos [5]. The visits aimed at collecting data on the degradation of tiles as well as on the prevailing environmental conditions that might have caused the onset of decay. The sites ranged from South Portugal (Alentejo) to the Northern Province of Minho. Degradation forms were classified as presumably resulting from damage caused by human action or mechanical interference of any form (that is, decay that would not have occurred in the existing conditions, if some form of interference with the tiles had not taken place), and decay that presumably followed manufacturing defects (that is, decay that given the existing conditions would necessarily occur because the tiles had an in-built weakness but would not if that weakness was not present). This last sort of decay was considered of interest to correlate with manufacturing defects detected by microscopic observation.

The method comprised microscopic observation of defects (both optical and electronic) and the simulation of decay through ageing tests with salt crystallization.

2.1- Observation by Optical Microscopy (OM)

Tile defects were studied by OM using both a binocular microscope Meiji- EMZ-TR and a petrographic microscope Zeiss Axioplan MC-100. However, it must be borne in mind that very thin cracking is not always apparent. The biscuits of early Portuguese tiles are usually of a very light colour, so as to avoid impairing the whiteness of the majolica, and thus the exact boundary between glaze and biscuit may be difficult to pinpoint by OM while the true extension and path of thin cracks is not easily disclosed (figure 4a) particularly when they propagate horizontally in the glaze-biscuit interface.

The use of penetrating inks may be helpful but may also be problematic because the biscuit has zones of spongy porosity that readily absorb ink without actually having any cracks (Figure 4b).

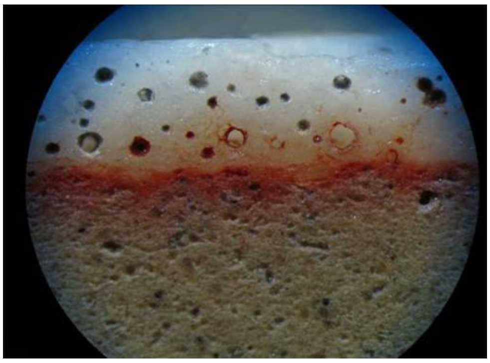


Figure 4a- Cracking systems are often confusing with optical imaging (a crack runs vertically with an almost invisible side branch under the glaze)...
… and (Figure 4b) inking may be misleading – lots of colour but no cracks here

2.2- Observation by Scanning Electron Microscopy (SEM)

SEM imaging provided an almost perfect means to complement optical microscopy in the mapping of defects, helping to understand the cracking paths through the glaze, into the biscuit, or in the glaze/ biscuit interface.

The width of the smallest cracks studied was of a few µm and so no great magnifications are needed for a research of this nature. Since the preparation of polished sections of glazed tiles was a new field to us, a comparative study was performed [6] and has shown that a standard polishing to 3µm was enough to ensure clear images. The specimen preparation method was as follows: fragile cracked specimens were vacuum impregnated with a resin and then cut, glued on to a glass slide and sectioned with a high-speed saw to a width of ca. 2mm. In this case no further impregnation was done after sectioning, so that all volumes filled with resin were originally accessed from the outside of the uncut tile sample. Polishing was done for 5+5 minutes with 9+3µm diamond abrasives. Specimens where thin glaze cracking was to be studied were further finished by a 5min hand polish using a 1µm diamond spray. This procedure was generally quick and gave satisfactory results.

The SEM used was LNEC's JEOL JSM-6400 with a X-ray EDS detector INCA X'sight from Oxford Instruments (figure 5).

Backscattered electrons (BSE) imaging was usually preferred because the lead-rich glaze is enhanced, ensuring clear boundaries. The samples were coated with Au/Pd (80/20) so that Carbon was only present in the sample and in the filling resin. The resin-filled voids show as very dark areas in the image and the use of EDS (X-ray mapping of C) can confirm that these are indeed filled with organic resin and are thus accessible from the surface of the glaze or from the side of the glaze-biscuit interface through paths that may, or may not, appear in the final sections. EDS X-ray mapping of Silicon was also used because that element is only absent from the voids and the resin-filled cracks.

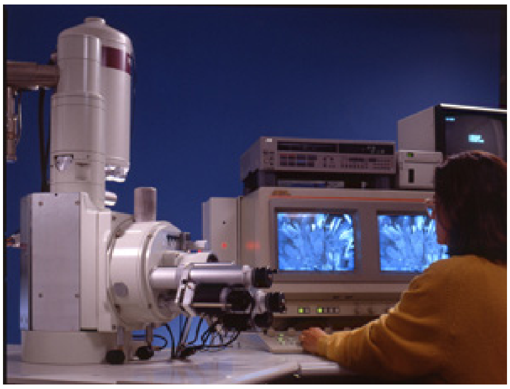


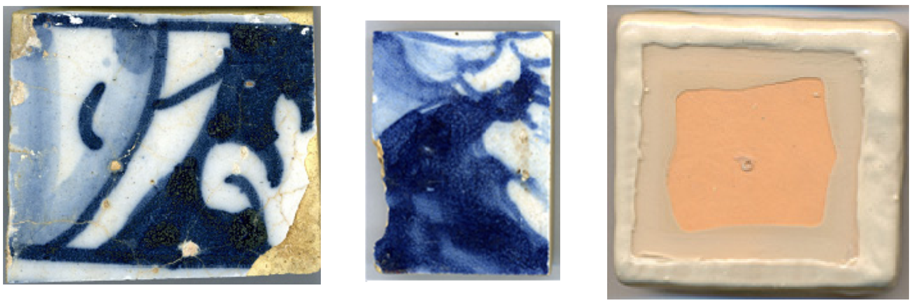
Figure 5- LNEC's JEOL JSM-6400

2.3- Ageing tests

Simulated ageing tests were performed through wet/dry cycles. A complete report on these tests and their results will be given in another medium, but a synopsis is necessary to this report.

Two sorts of samples were prepared for test: Type I- small ca. 35-45 sq.cm pieces were cut from azulejos - these were chosen so that the glaze area would include the defect to be studied; and Type II- squares of biscuit of approximately 50 sq.cm over which 0.74 mm thick glass was glued with epoxy resin in a way that simulated defectuous glazed tiles. Figure 6 illustrates some of the samples.

The test protocol was very simple: the lateral surfaces of all samples were made water-tight with epoxy resin and the sample fully wetted with a 3:10 wt/wt solution of sodium chloride. After wetting, the back side of the samples was isolated with plastic film glued with mastik so as to force evaporation through the glaze side. Type I samples were then let dry for as long as it took in a ventilated oven at 60ºC. After drying, any new damage was noted and the cycle repeated. The wetting cycles after the second were done with deionised water. Type II samples were subject to just one drying cycle at 40ºC after imbibition in the saline solution.



ia) ib) iia)

Figure 6- A selection of Types I and II samples for study through artificial ageing tests by salts crystallization.

3- CRAZING

3.1- Microscopic study

When a tile cools after the second firing and if the thermal expansion coefficients of the glaze and the biscuit are not finely tuned, the glaze top may contract substantially more than the biscuit. Then the ceramic body exerts through the interface a homogeneous traction on the glaze. Glass cannot respond elastically and will crack. The fissures propagate sideways, until a crack meets another at an app 90º angle, and vertically until the tension is relieved [7]. This situation leads to *crazing*, the formation of a cracking pattern in the glaze resembling drying mud and often referred by the French designation *craquelé*. Visually, the pattern seems formed by odd trapezoidal polygons with similar dimensions (figure 7).

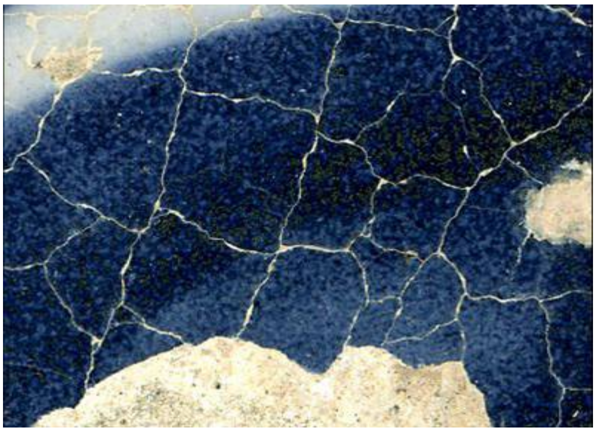


Figure 7- A pattern of crazing highlighted by efflorescence

Since crazing results from an incompatibility between physical characteristics, it would seem that whenever a tile is crazed, all tiles from the same manufacturing cycle will be crazed as well, and so all tiles in a panel must show *craquelé*, whenever one does. But that is not the case, because crazing can occur in other situations, even when the thermal expansion coefficients of the body and the glaze are compatible. When, after the firing of the glaze, tiles are cooled too hastily, the glaze will contract immediately while the biscuit, having a much larger thermal mass, will have a delayed response. And so, crazing may occur during cooling even though it might not have occurred had the cooling been slower. For that reason, some tiles that cooled faster may be crazed, while others are not.

There can also be a delayed crazing caused by moisture intake. When tiles are wetted, and particularly when tiles that are applied to the walls suffer cycles of wetting and drying, the biscuit will expand due to the intake of water, but the glaze will not take any appreciable amount of water and thus the body will apply on the glaze a homogeneous traction that may result in a crazing pattern. Although in this case crazing occurs months, years or even decades after manufacturing, it may still be considered as a result of the manufacturing process because, as was recognized since the phenomena involved were understood, a good fit is one where in normal conditions the glaze is in slight compression so that the wetting of the biscuit will result in a state nearing a null interfacial stress.

Crazing is, thus, a widespread phenomenon with several possible remote causes but only one apparent result: the formation of the characteristic tile-pattern. However a microscopic study reveals the occurrence of two very different cases: one where the cracks cross the glaze-biscuit interface vertically and propagate forward into the body; and one where once the interface is reached the cracks change direction and propagate transversally through the interface. There are also cases of mixed propagation where the stresses are relieved through both a vertical and an interfacial propagation.

On another medium our group disclosed the results of a simulation of azulejo crazing [4] with a numerical model based on a Delft lattice [8] on a MATLAB environment. The simulation predicted that, when the bond between the glaze and the biscuit is considerably stronger than the cohesion of the biscuit itself (as is often the case) the cracks originating in the glaze will initially propagate vertically into the biscuit, eventually with side branches inside the ceramic body in bad cases of crazing. When, however, the bond between glaze and biscuit is relatively lower than the cohesion of the biscuit, the cracking will follow the path of less resistance under the glaze and detach it locally from the biscuit. The SEM-based research confirmed the predictions and further gave evidence of the paths followed and of cases where both kinds of propagation co-exist in the same tile.

Figure 8 shows the path of vertical propagation of individual crazing cracks in one of our samples. This is the simplest case, where cracks propagate down for a length that does not usually exceed double the glaze width, without branching. We named these: *Type I* crazing cracks.

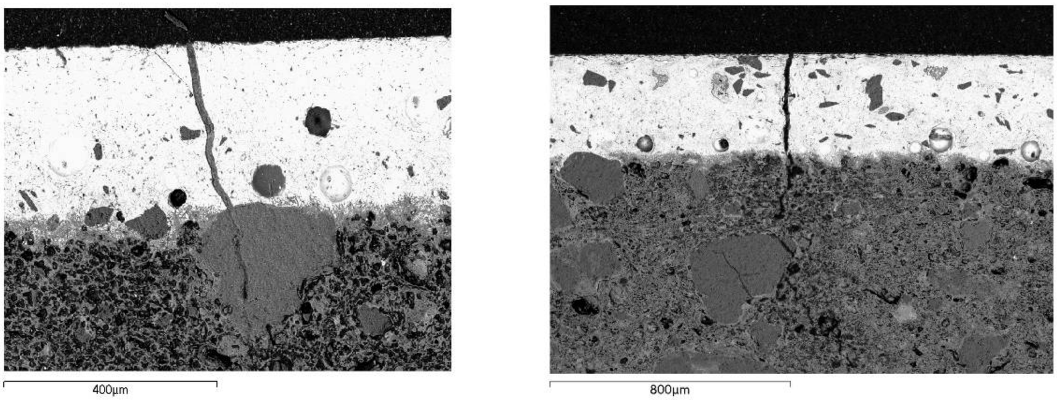


Figure 8- BSE images of an azulejo cross section showing crazing cracks propagating vertically into the ceramic body (sample Az02/07)

Figure 9a shows crazing in a case where the cracks propagate into the biscuit but mostly in the glaze/biscuit interface (the slide was prepared from a sample of the tile illustrated in figure 7). The SEM images clearly show the vertical development of the crack that distorted a gas bubble, propagating sideways under the glaze. Using the fact that the impregnation with resin filled the accessible voids, figure 9b depicts an X-ray map of Carbon, marking positively the path into the biscuit, and figure 9c a similar map of Silicon, which is a negative marker of voids and often shows the cracking patterns in a more clear way. We named these: *Type II* crazing cracks.

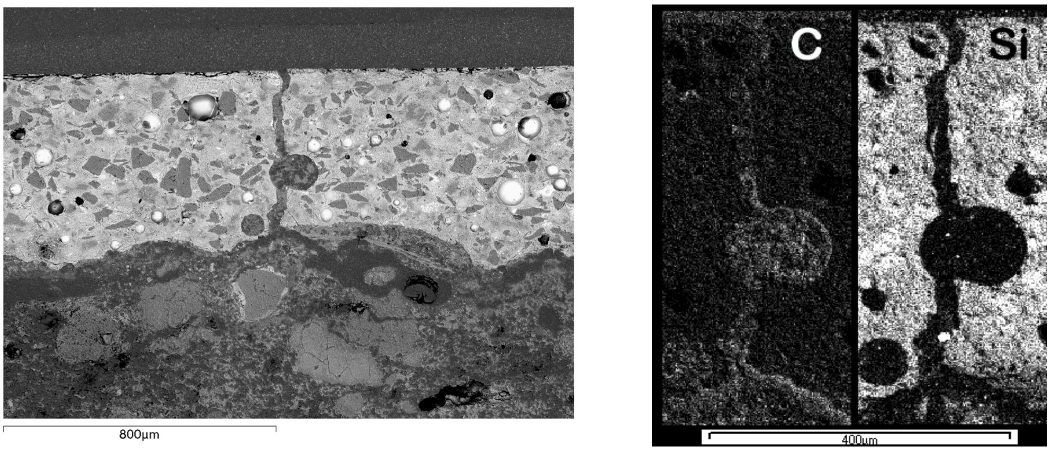


Figure 9a- BSE view of a crazing crack propagating in the glaze/biscuit interface and close-up X-ray maps of Carbon (9b) and Silicon (9c)- sample Az02/06

Not all tiles craze down, either into the biscuit, or else sideways under the glaze. In some, both paths offer routes of similar resistance and thus cracks propagate both down and sideways. Figure 10 illustrates two views taken on a single tile illustrating the double path.

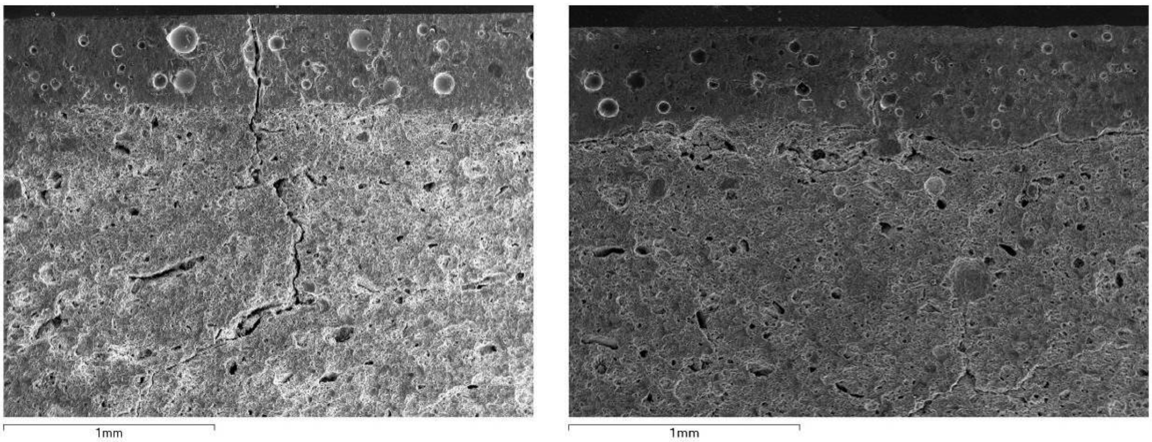


Figure 10 – SEI images of sample Az02/11 showing crazing cracks propagating down into the biscuit with side branching (9a) and sideways into the glaze/biscuit interface (9b)

In the particular case of the tile illustrated in figure 10, the biscuit had a confusing BSE image and so it had to be polished for 5+5 minutes with 1µm diamond grit and secondary electron imaging (SEI) had to be used to achieve an acceptable result. This particular tile was ultimately seen to have a cracking system that actually spanned its whole width at some spots and was widely colonized by filamentous fungi. The cases of mixed propagation like this one must be considered as Type II crazing because, as shall be shown next, that is the type resulting in a more immediate risk to the preservation of the tile.

Whenever salt crystallization occurred on the sites we visited, two cases were recognized which correspond to the two kinds of crazing. The Type I “vertical crazing” as illustrated by figure 8 offers a direct route from the biscuit outwards which, when the cracks are open and soluble salts are present, results in a pattern of efflorescence highlighting the glaze cracks (figure 11). Several similar cases were seen and, whenever possible, documented with the same outcome: although efflorescence confirms the evaporation of moisture from the walls, there was no actual decay in terms of macroscopically recognizable glaze loss directly attributable to the crazing. In figure 11 some areas of glaze loss are clearly visible but they pertain mostly to the edge areas where crazing is not even apparent.

Figure 11- Efflorescence in a crazed tile
(Coimbra Old University- photographed 2008)

Type II crazing that propagates horizontally is a different matter altogether. Since it runs into the glaze-biscuit interface, it causes a partial delamination of the mosaic patches of glaze. And so Type II crazing as illustrated in figure 9 originates a mosaic of “glaze islands” that are already partly detached from the biscuit. The hidden crystallization of salts or any other physical process causing shear stresses in the interface (moisture or thermal cycles, or maybe even vibration) may conceivably contribute to the propagation of damage resulting in a patchy mosaic-like detachment (figure 12). In this form of decay, a clean relatively smooth biscuit surface results with a characteristic polyhedral glaze boundary resulting from the detachment of full crazing “islands” or parts thereof. Often this sort of crazing is also highlighted by efflorescence, particularly whenever the loss of glaze is yet minimal, but it will likely, in time, lead to glaze detachments and thus calls for remedial measures without which all the glaze may eventually be lost.

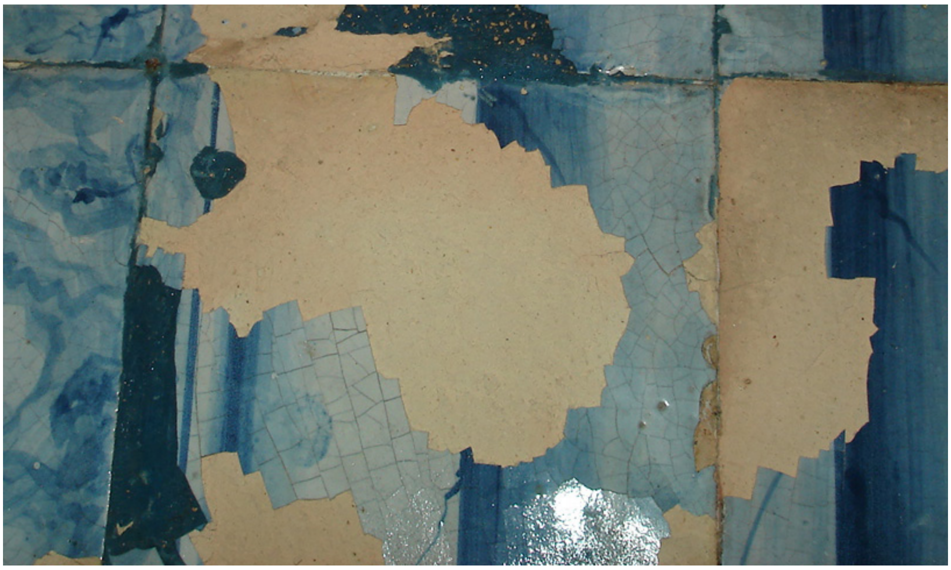
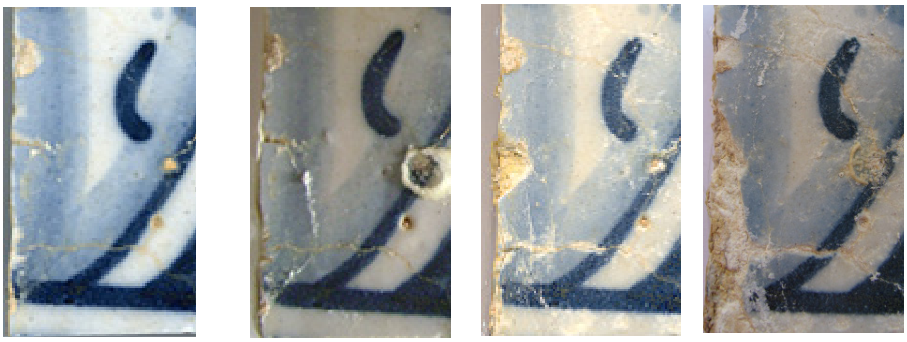


Figure 12- Delamination of the glaze from the biscuit in a severe case of Type II crazing (Igreja dos Terceiros de S. Francisco, Viseu- May 2010)

3.2- Ageing tests

We simulated the decay of tiles with crazing in the laboratory through accelerated ageing tests with salt solutions, as described in Chapter 2.3, obtaining the detachment of one of the glaze mosaics at cycle #3 in a sample cut from the tile illustrated in figure 7 (see figure 13), with new detachments starting to be apparent at cycle #4.



a) b) c) d)

Figure 13- Delamination of the crazed glaze from the biscuit after cycles of accelerated ageing with sodium chloride solutions, as described in Chapter 2.3. a) before the saline solution imbibitions; b) after 1 cycle, c) after 3 cycles, d) after 4 cycles.

4- GLAZE DELAMINATION BY SHIVERING

4.1- An introduction to shivering

A less known but potentially more noxious manufacturing defect than crazing is *shivering*, which stems from the opposite situation: the thermal expansion coefficient of the glaze is not tuned to that of the biscuit in a way that during the cooling phase, after the second firing, the ceramic body contracts considerably more than the glaze. Due to the resulting compression tensions, the glaze may suffer small nicks on the edges or detach from the biscuit (glaze *delamination*). The results of a numerical simulation done as mentioned in Chapter 3 [4] has shown that, due to the arising stresses, in a flat tile the damage starts near the edges where the glaze may separate locally from the body and break, cause a sloping cracking of the biscuit or, indeed, even propagate to the centre of the tile resulting in extensive detachment patches (figure 14). In irregularly surfaced tiles, the glaze will tend to form a chord of any arch and thus conceivably delaminate locally anywhere in the glaze area. The lower the adhesion between glaze and biscuit, the less the degree of thermal retraction incompatibility needed to result in delamination by shivering.

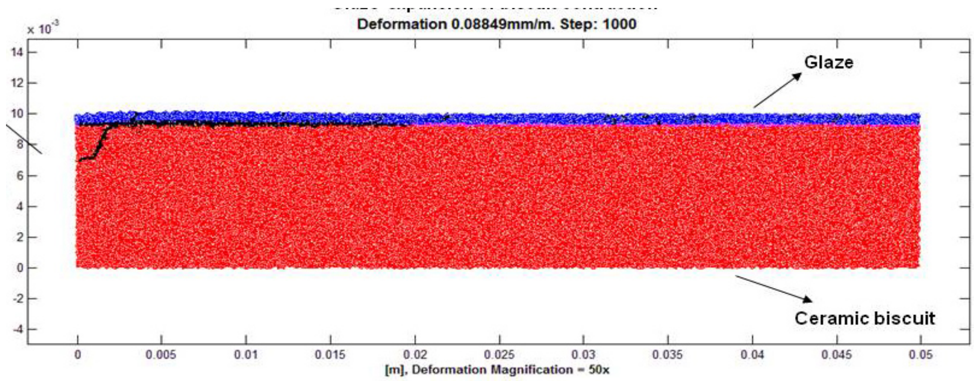


Figure 14- One step of the graphic result of a numerical model of a propagating glaze delamination (black fracture crack) in a cooling tile subject to shivering
(numerical model by Miguel Abreu, image taken from [4])

4.2- Microscopic study

Figure 15 depicts a section across a shivered tile with delaminated glaze, showing the wavy crack which results from a dimpled fracture surface, demonstrating that it propagates through the biscuit, only occasionally touching the glaze. This means that in the typical shivered tile, the glaze will fall off with adherent biscuit, forming dimples that are clearly seen and felt, while a clean detached glaze may point to a different problem (lack of glaze/biscuit adhesion with or without concomitant shivering).

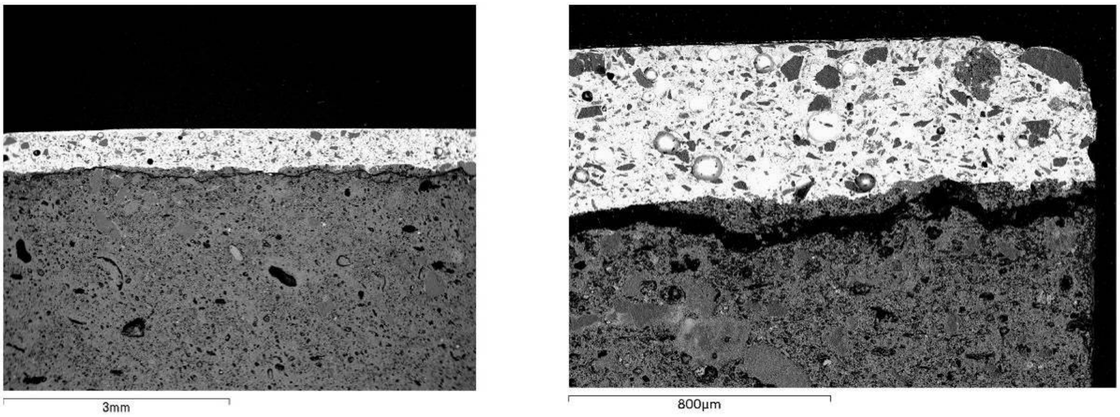


Figure 15- SEM (BSE) images showing the glaze delaminated by shivering depicting the characteristic wavy morphology corresponding to the sectioning of a dimpled shear fracture and its propagation almost exclusively through the ceramic body

Figure 15 illustrates a case where the delamination goes right to the edge of the glaze. In this case, any moisture with dissolved salts would evaporate near the exit and crystallization would commence near the edge and “lift” the glaze from there. The glaze loss would typically progress from the edges, and this is likely the cause of a typical morphology of decay in which the glaze loss progresses towards the centre of tiles, often with a pattern of cracking of the remaining glaze that follows the border of the lost area (which we call *a delamination front*) and marks the next pieces of glaze that will fall down. Figure 16 illustrates the typical morphology of a panel decaying in such a way, whose tiles were probably more or less delaminated to the edges as a consequence of a faulty manufacture.

Figure 16 – A typical decay morphology probably indicating that the tiles were initially shivered to the edges (Viseu Cathedral- May 2010)

Examining figure 16 more closely, half a dozen spots will be noticed in which the glaze loss does not actually go to the edge, but rather makes up a round lacuna somewhere inside the glaze. The situation is exemplified by the tile in figure 17.

Figure 17- 17th century tile with a round lacuna inside the glaze area

This case corresponds to shivering delaminations which only affect an area inside the glaze and do not go to the edge, as exemplified by the longitudinal cut of figure 18. It is an important cause of decay, as will be seen next.

Figure 18a- Part of a longitudinal cut in a shivered tile showing a glaze delamination over a recess that does not reach the edges (marked by a grey line); 18b- detail under the optical microscope

The situation illustrated in figure 18, though alarming, may go unnoticed for decades or even centuries if the azulejo panels are on dry walls. But when the walls are wet, the biscuit will absorb moisture and expand, while the glaze does not. When the expansion of the ceramic body overcomes any residual compression that the glaze may retain, the glaze will be put in traction and eventually crack. When the biscuit dries and contracts, the glaze will lift. Eventually pieces will break off.

When the glaze has pin-holes (figure 19) these provide an evaporative route to the water wetting the ceramic body. If that water contains soluble salts, as it in general does, crystallization will occur under the pin-hole, in the empty space between the biscuit and the glaze. The agglomeration of salt will eventually start lifting the glaze, forming a bubble that, in time, breaks resulting in an immediate roundish lacuna that may have an area exceeding 1 sq.cm. Whenever delaminated glaze remains at its boundaries, the process will proceed and the lacuna will slowly widen until most of the glaze is lost (figure 20a, b).

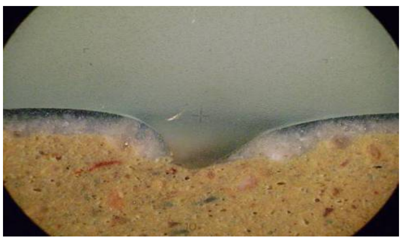


Figure 19- A pin-hole through the glaze provides a direct evaporation route from the ceramic body to the exterior

As said before, such cases need the previous occurrence of shivering delamination and a pin-hole through the glaze. After the lacuna is formed, the imprint of the original pin-hole can sometimes be recognized on the remaining biscuit, often with rings of salt crystallization around it, giving testimony of the process that lead to it (see, for instance, figure 20 a).

Figure 20a- Typical glaze loss through efflorescence under a shivering delamination (the position of the evaporation pin-hole is imprinted on the ceramic body) and (20b) grazing view of another area of the same panel making the delamination apparent (Madre de Deus Convent, Lisbon- July 2009)

4.3- Ageing tests

Shivering is an insidious manufacturing defect that, given the proper conditions, may lead to extensive glaze losses in a relatively short lapse of time and so this case, quite common but, to our knowledge, misunderstood and as yet undescribed in scientific literature until now as a source of decay of azulejos, has been of considerable interest to us. We simulated this phenomenon in the laboratory through accelerated ageing tests with salt solutions, both on the naturally delaminated tile shown in figure 18a and in simulated tiles made from thin sheets of glass with pin-holes across that were glued on their periphery to ceramic bodies (as described in chapter 2.3 and shown in figure 6). On both cases the bubbling behaviour was observed, eventually leading to the loss of considerable areas of glaze in a single detachment event. Some results are illustrated in figures 21 and 22.

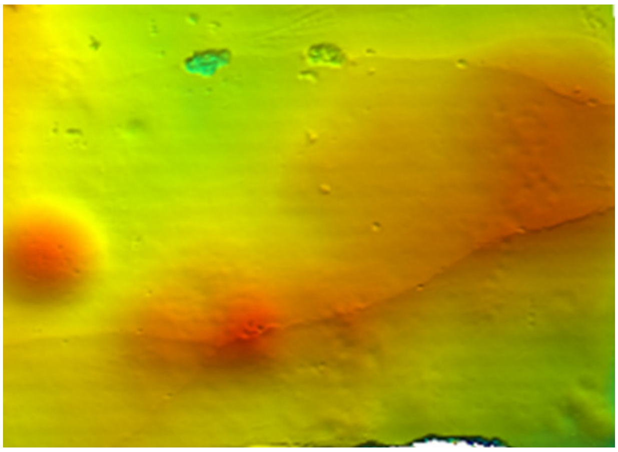


Figure 21- 3D optical surface profile of a sample of the late 17th century tile of figure 18 after two cycles of accelerated ageing as described in Chapter 2.3. The raised area of delaminated glaze and its breakage are evident.

Figure 22- Evolution until breakage of a simulated glaze delamination with a through pore, during time, while drying at 40ºC after one imbibition with a sodium chloride solution.

5- FERRUGINOUS GLAZE STAINING

It is well known that any section in the glaze of an azulejo shows a large density of bubbles of all sizes, some of which may eventually occupy most of the glaze width. Figure 23 was obtained in a non-impregnated and barely polished sample, for illustrative purposes only. The likeness to spheres is misleading because actually the sectioned bubbles are only empty caps.

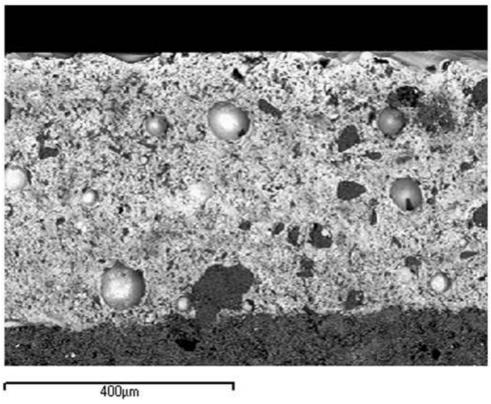


Figure 23- Glaze bubbles in an azulejo (BSE)

Bubbles were considered undesirable in fine majolica work, as in china, because they may detract from a spotless white surface appearance and there are actually old writings on how to avoid them. But they may have been viewed positively by azulejo makers as the cheapest of opacifiers. Tiles are often found with a speckled look, totally detracting from the ideal white ground of majolica (figure 24). Under optical magnification, the brownish colour often resolves into spots and a cut section quickly confims that the colour derives from a substance filling the bubbles, spreading outwards, and imparting a rusty colour (figure 25).

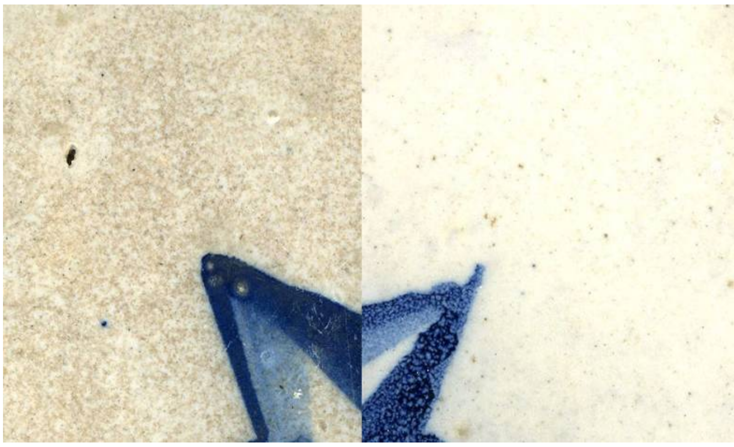


Figure 24- A tile affected with a pathology that stains the white majolica compared to a sound tile

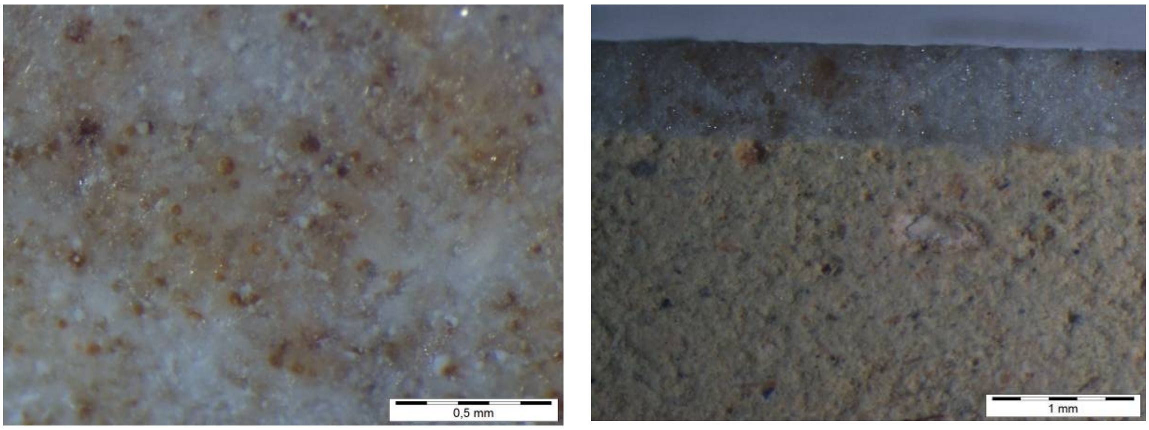


Figure 25 – Microscopic images of a stained tile seen from the top (25a) and in section (25b)

The fact that some tiles in a panel are affected by this pathology while others seem immune to it (as happens, for instance, at Palacio Pimenta in Lisbon, where the kitchen azulejo cover shows a chequered pattern of stained and sound tiles) and noticing that if affects most often azulejos of cheaper production and a more recent manufacture (late 18th and 19th centuries) lead to the notion that it too derived from some manufacturing defect that made the glaze more permeable than is usually the case and afforded paths from the exterior to the interior of the glaze bubbles.

A simple check was performed on samples prepared for SEM work that were purposedly not re-impregnated after cutting. Then, any bubbles filled with resin have to have been filled from the exterior, even if the entry path is not evident in the final section used for viewing. Figure 26a depicts an example in secondary electrons imaging (SEI) in which the resin-filled bubbles are conspicuously black. Figure 26b shows the same in the so-called topographic mode (BSE-TOP), in which those resin-filled bubbles come out flat contrarily to those that are not connected to the glaze surface and show as caps. Finally figure 26c depicts the X-ray map of Carbon in another area of the same slide in which three bubbles near the glaze/biscuit interface are seen to be filled with resin and thus prove to be connected to the surface of the tile.

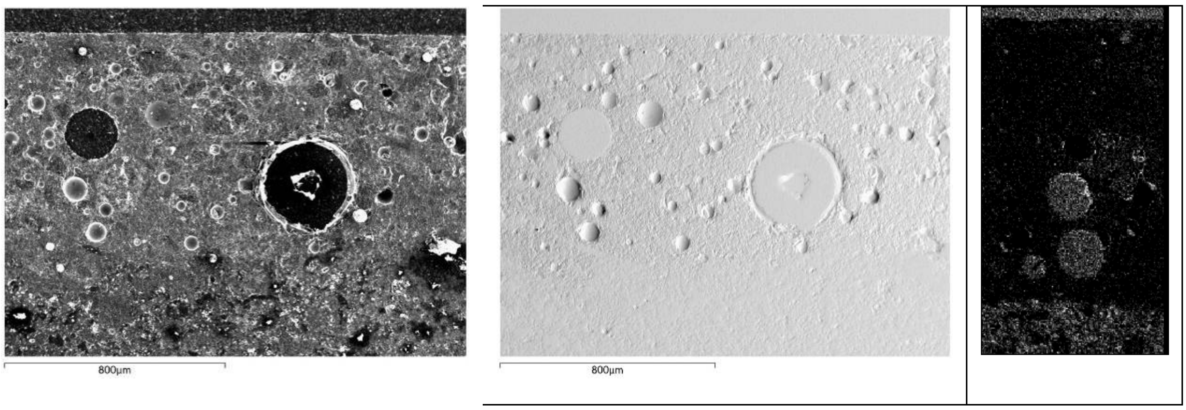


Figure 26- Those bubbles accessible from the surface (and potentially stained with a brownish inclusion) can demonstrably be filled from the surface with impregnating resin and clearly distinguished in SEI (left), BSE-TOP mode (center) and in an X-ray map of Carbon of another area of Sample Az02/03

6- CONCLUDING REMARKS

Although a wall wet with infiltrations carrying soluble salts is the near cause of decay of many historic Portuguese azulejo panels, there are insidious far causes stemming from an array of manufacturing defects that were, so to say, built-in and subsequently lay in waiting for conditions favourable to the onset of decay. The understanding of this fact is of the utmost importance for conservation work.

It is not enough to reintegrate lacunae: when dangerous tile defects are present they must also be addressed, even when hidden, for a restoration to be durable. If preventive interventions are considered, it would be of capital importance to detect those defects that render tiles fragile so as to make it possible to apply corrective measures to ensure, as far as technologically possible, that the concurrence of factors leading to decay is avoided at all times for the sake of preservation of the heritage values.

The survey of decay forms on relevant heritage sites together with the microscopic study of manufacturing defects on Portuguese azulejos and laboratory simulations allowed relating decay with some defects and understanding how a situation originating centuries before may, much later, lead to decay and often total loss of the painted glazed layer when certain adverse conditions occur.

The knowledge achieved is now being used on a larger research programme to simulate the several situations in the laboratory, where the parameters may be controlled, aiming to confirm hypotheses and improve the scientific knowledge about azulejos and hopefully contributing, in the near future, to the full understanding of the onset of decay. This will foster the development of counter measures allowing to intervene on the decaying panels, as well as on those at risk, to help ensure the full longevity that glazed tiles were supposed to enjoy.

Acknowledgements

SEM / EDS operator : Ana Paula Menezes

Preparation of slides with polished sections: Luís Figueiredo Nunes

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