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Ancient Wall Tiles – The Importance of the Glaze/Ceramic Interface in Glaze Detachment

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One of the most severe pathologies suffered by early industrially produced tiles in Portugal in late nineteenth century is glaze detachment in wall tiles placed in the lower part of the façade. It is known that salts crystallize provoking the glaze detachment, destroying the waterproofing and the beauty of the wall tile and this is one of the crucial factors towards this occurrence.

The present work questions the importance of the thickness of glaze/ceramic body interface, in what concerns glaze detachment provoked by salt crystallization. SEM-EDS was used to perform all the observations that lead to the conclusion that the exuberance of the interface between glaze and ceramic body has no influence in the resistance of the glaze to salt crystallization though time, being the porous network more determinant.

Keywords: ancient wall tiles, glaze/ceramic body interface, salt crystallization, glaze detachment.

1. INTRODUCTION

For centuries, wall tiles have been used for decorative reasons or because they supply a durable and waterproofing facade finishing. This ceramic element is composed by two ceramic entities whose degree of interpenetration depends on their raw materials and firing enthalpy – the ceramic body and the glaze. The ceramic body is the mechanical support for the waterproof and decorative part: the glaze with decoration. It is known that salts crystallize provoking glaze detachment, destroying the waterproofing of the wall tile as well as its beauty [1 – 6]. With the wetting/drying cycles natural of years passing by, salts present in ground water and in the mortar, dissolve and precipitate in the porous ceramic body structure. If the mentioned crystallization happens to close of the glaze/ceramic body interface and the provoked stress upon the structure is big enough, the bond of the interface with the ceramic body collapses. Glaze detachment appears. All these findings were analized with SEM/EDS.

Since remote times, lead glazes have been used in tiles due to their bright finishing and low melting temperature. The lead glaze is a mixture of lead compounds and silica that, after melting, become a transparent shinning surface. In order to cover the colour of the ceramic body that usually was not white a small percentage of tin was added to the lead glaze in order to transform it into a white and opaque glaze. To the former glaze many cations could be added as colorants (Cu, Co, Mn, Fe, etc.), each of them promoting a different colour [7].

The glazes under study are lead-rich, tin-opacified and were applied in a biscuit-fired body, previously fired at a higher temperature (around 1100 °C). During the glaze firing process, liquid phase is promoted due to fluxes and to the low lead melting point, penetrating into the near-surface ceramic body pores and reacting with the ceramic body minerals forming a zone of chemical digestion that is a mix of both bodies and called the interface zone. This layer is composition, time and temperature dependent [7, 8]. The thickness of this layer is given by time/temperature binomial allowing, or not, the diffusion of elements between glaze and ceramic body [9, 10]. A study made to Italian majolica from 15th to 17th century [11] revealed that the interaction between the glaze and the ceramic body had about 20 µm to 30 µm, to give an idea for comparison purposes although the regional variations of compositions and firing temperatures/cycles.

Studies made about the importance of the interface glaze/ceramic body reveal that the more effective the formation of the interaction layer between ceramic body and glaze, with an intermediate chemical composition due to diffusion of elements, the higher the glaze resistance to thermal shock, crazing and frost resistance [9, 10]. As glaze detachment caused by salt crystallization is a too frequent pathology in old wall ceramic tiles, placed in humid areas of the façade (normally closer to the ground), the question about the importance of the magnitude of glaze/ceramic body interface remained to be answered.

The aim of the present study is to understand how important this bonding layer is, if it really dictates glaze durability in terms of glaze detachment caused by salt crystallization in the porous ceramic body structure. For that, SEM/EDS mapping and quantification techniques were used. Mapping allows tracing the relative quantity and localization of the existing elements in the sample.

2. MATERIALS AND METHODS

To the present work five samples of ancient tiles were chosen (five tiles from the left side of Table 1) due to their diversity of results in the subject under study. All the samples are from Portuguese buildings from the late 19th and early 20th century, suffering from glaze detachment caused by salt attack in the lower part of the façade [12]. The upper parts of the façades present no glaze

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detachment. A modern tile (HC) was analyzed in order to have an idea of nowadays interface thicknesses.

Table 1. Tiles pictures and references

Ref.	P24	P89	P104	P127	P133	HC
Oporto Tiles 19th century						

To enable the visualization of glaze/ceramic body interface, vertical cuts with 1.5 cm long and 0.5 cm height were made in the tile with a sharp mechanical cutting machine, obtaining the simultaneous observation of the glaze, glaze/ceramic body interface and ceramic body. The samples were mounted in resin and polished with 30, 15, 9, 6, 3 and 1 µm diamond pulp until a smooth surface was obtained. Due to the fact that samples of ceramic body suffer easy desegregation in the polishing process, in some samples it was not possible to reach an even surface.

A high-vacuum scanning electron microscope (SEM) Hitachi SU-70 with 1 nm resolution was used, equipped with energy-dispersed spectroscopy (EDS) Bruker Quantax. Also a Hitachi 9400 was used in some samples. An acceleration voltage of 15 kV was used for observation and measuring the interface and 30 kV for qualitative and quantitative element mapping. For EDS calculations purposes an 110 µm × 25 µm area was considered in the samples with measurable interface. In the samples were the average interface thickness is narrower than 25 µm, the elements values were obtained in the found thicker parts of the interface.

Glazed tiles were tested to determine water absorption according to EN ISO 10545-3: Determination of water absorption of open porosity, with ±0.1 % accuracy [13].

Pore dimension by mercury intrusion was performed in small ceramic body pieces using a Micrometrics AutoPore IV apparatus that allows the measurement of mercury intrusion pore diameter of 5.5 nm to 360 µm.

3. RESULTS AND DISCUSSION

From all the samples elemental mapping and elemental quantification were performed (comparisons between them can be made, as data was collected in the same conditions). SEM images and mapping can be seen in Figure 1.

P127 has crazing problems due to shear forces that are promoted by a big difference between ceramic body and glaze expansion linear coefficient that is why the glaze presents cracks and sample has not an even look.

Tables 2 to 4 shows the values of the most significant elements present in the glazes near the interface region of the studied samples. It also displays the composition of interface area and of the ceramic body near the interface region. The presented values were acquired by EDS.

Analyzing EDS elemental mapping in Figure 1 and element quantification in wt% in Table 2 to 4, it seems that when there is the development of an interface there are elements present like silicon, lead, potassium, aluminium, sodium and calcium. Those elements have contributions both from the glaze and the ceramic body. The presence of lead in the interface must depend on the glaze firing cycle, glaze melting point and open porosity of the ceramic body. From mapping it may be seen that the only element that diffuses beyond the interface area is potassium. Sodium and alumina are the elements that stand out in interface composition (Table 5).

Table 2. EDS wt% values of the chemical elements present in the glaze of the studied samples

	Si	Pb	K	Al	Na	Ca	Sn	O and others
P24	20.7	19.7	5.2	1.0	0.2	–	4.1	49.1
P89	24.9	16.7	8.3	2.2	0.3	1.0	–	46.6
P104	26.4	12.1	8.6	2.9	0.4	0.5	–	49.1
P127	21.5	24.5	5.4	1.9	0.9	0.7	–	45.1
P133	20.6	26.5	6.7	2.5	0.5	1.6	–	41.3

Table 3. EDS wt% values of the chemical elements present in the interface of the studied samples

	Si	Pb	K	Al	Na	Ca	Mg	O and others
P24	–	–	–	–	–	–	–	–
P89	18.8	–	10.7	10.8	1.2	9.6	0.2	48.7
P104	18.4	2.2	1.5	15.7	2.0	10.9	0.3	49.0
P127	20.6	2.5	4.0	9.0	2.2	9.0	0.4	52.3
P133	20.8	4.4	6.5	9.9	2.9	7.9	0.2	47.4

Table 4. EDS wt% values of the chemical elements present in the ceramic body of the studied samples

	Si	Fe	K	Al	Na	Ca	Mg	O and others
P24	12.1	8.8	–	6.6	0.2	33.0	0.9	38.4
P89	16.2	3.4	0.9	6.8	0.6	16.0	1.9	54.2
P104	17.2	1.8	1.0	10.4	1.0	14.7	0.2	53.7
P127	18.2	1.5	2.5	12.6	2.7	9.7	0.1	52.7
P133	15.9	3.4	0.6	7.6	0.6	18.3	1.9	51.7

In Table 5 the interface area elements of P133 can be seen (in the middle of the images), showing a pronounced concentration of Al, Na and K in that area, comparing to the glaze and ceramic body´s, revealing element migration both from the glaze and the ceramic body to the interface.

Table 5. Elementary EDS images of P133 (Al, Na, K)

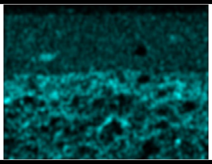
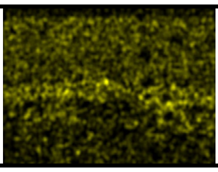
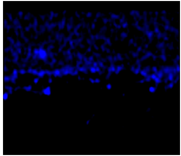
Al	Na	K
		

Table 6 shows the average of 5 different measurements made in the interface of each sample.

In Table 6 it can be seen that samples present interfaces width variations, from a no measurable interface until about 54 µm. When cutting P24, which has an interface that is not measurable, it could already be seen that glaze peeled off on the saw cutting path, revealing a deficient glaze/ceramic body interaction.

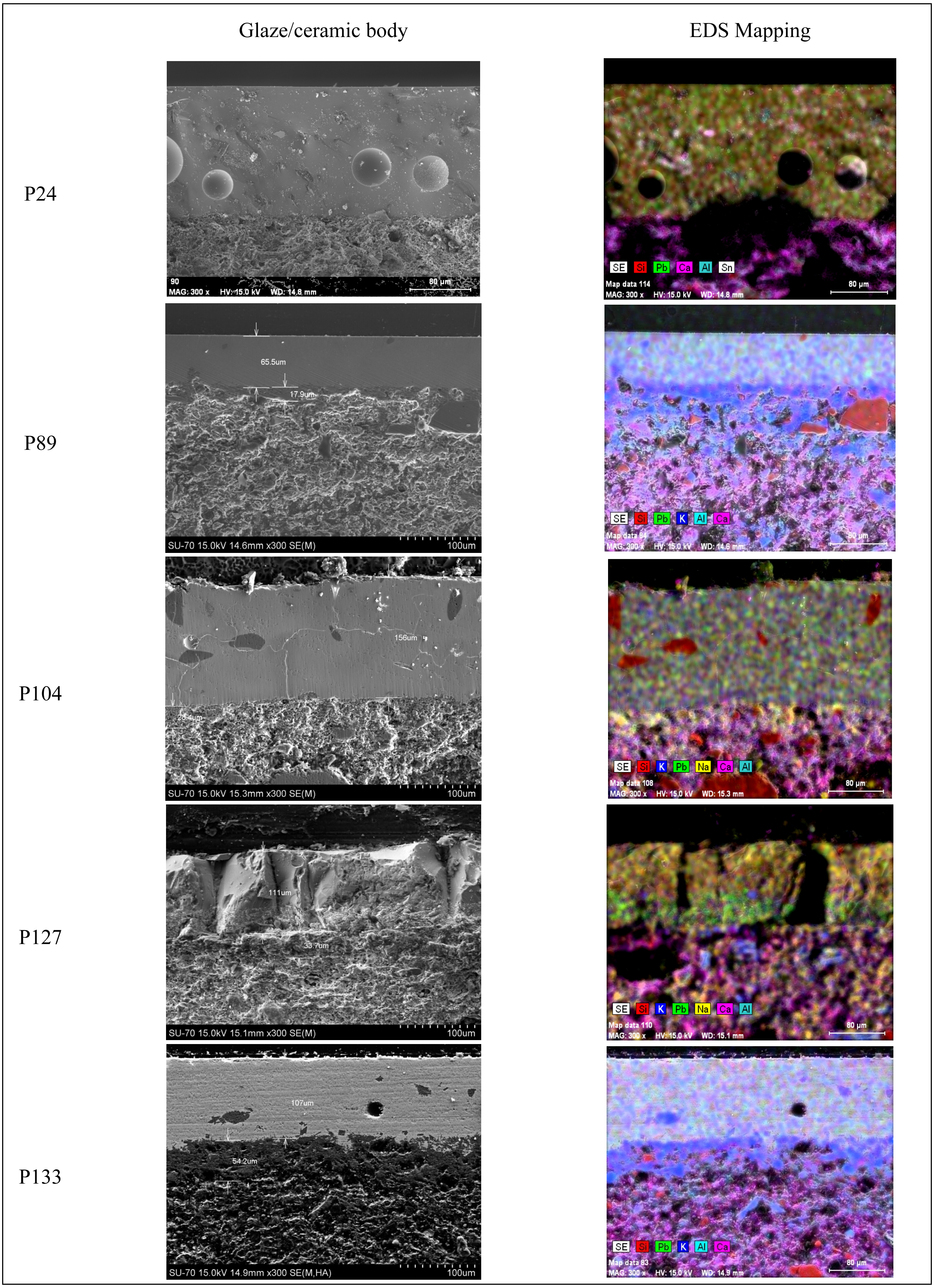


Fig. 1. SEM/EDS images and elemental mapping of the glaze, interface area and ceramic body from the studied samples

Table 6. Average interface values observed

Tile reference	Average interface observed [µm]
P24	Not measurable
P89	17.9
P104	28.4
P127	33.7
P133	54.2

In order to have a comparison term concerning glaze/ceramic body interface, this feature was analysed in a contemporary tile used in restoration as a pictorial replica. As can be seen in Figure 2, the interface has a mean value of about 18 µm. As modern tile production is more controlled and stable than 100 years ago, it is considered that the interface value found in this contemporary tile is representative within its brand

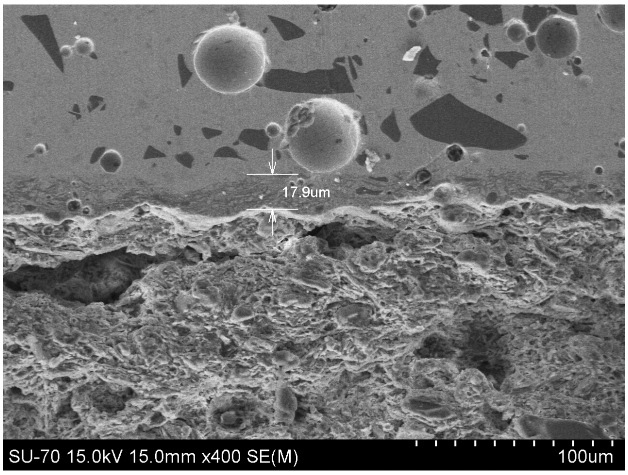


Fig. 2. SEM image of interface glaze/ceramic body of a contemporary tile (HC)

As all the samples suffered from glaze detachment caused by salt crystallisation only in the lower part of the façade, this suggests that these physical mechanisms are important enough to destroy what at first impression could seem a safe bond (54 µm interface), comparing with the value found in the modern tile. Far from salt attack, tiles hold without glaze detachment the passing by of one hundred years.

Hydration/dehydration of the supporting mortar, transports to the tile ceramic body soluble salts that crystallize in its pores, causing stresses big enough to cause the ceramic body breakdown [4, 5, 14, 15]. As in the interface between the ceramic body and the glaze, the porosity decreases abruptly, it is expected that crypto-florescence will appear just beneath the interface. In the studied old ceramic bodies, high pore volume and considerable suction ability (promoted by the small pores), favour fluid circulation within its microstructure leading, inevitably, to deterioration [4, 16 – 19].

The pore dimension by mercury intrusion determination was performed in the 2 old tiles with the bigger water abortion percentage and in the contemporary one. The old tiles under study have calcareous ceramic bodies with high open porosity (Table 7) and most of the pores have less than 1 µm size (Figure 3). In comparison, it can be seen that the modern tile (HC) has less water absorption and larger pores. The porosity features of the old tiles make them more prone to chemical and mechanical destruction by wetting/drying cycles promoted by weathering [19].

Table 7. Water absorption of the studied samples

	P24	P89	P104	P127	P133	HC
Water absorption [%]	21.6	20.8	18.1	22.0	22.6	14.7

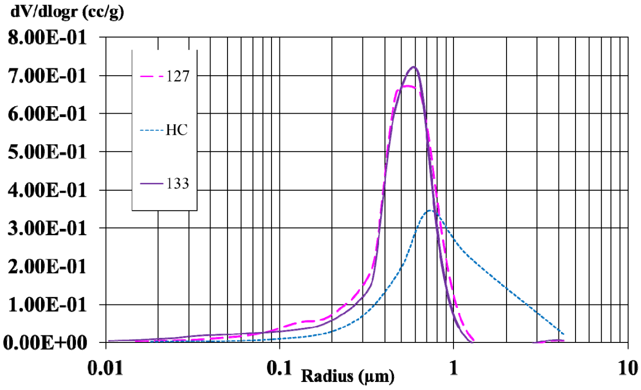


Fig. 3. Volume of mercury intrusion data in 3 samples (P127, HC and P133)

A tile suffering in some areas from glaze detachment was cutted and analysed by SEM, were it can be seen the glaze and the ceramic body in cross section. It was seen that the fracture that initiates the glaze detachment happens beneath the interface area, in the ceramic body, probably because porosity is the weakest part of the system (Fig. 4).

Analysing closely a damage interface, crystals can be seen occupying porosity underneath the glaze/ceramic body interface (Figure 5). In Figure 6, it can be seen the crystal EDS that is marked with a cross in the photograph of Figure 5. Analysing the EDS it cannot be forgotten that the signal from what is underneath is also captured by the EDS sensor. Besides having the elements of ceramic body composition, it can be seen a chlorine peak.

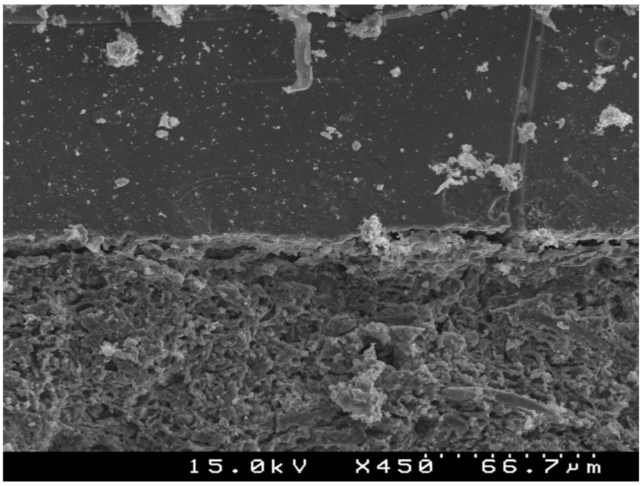


Fig. 4. A SEM cut view where can be seen a fracture beneath the glaze of P133

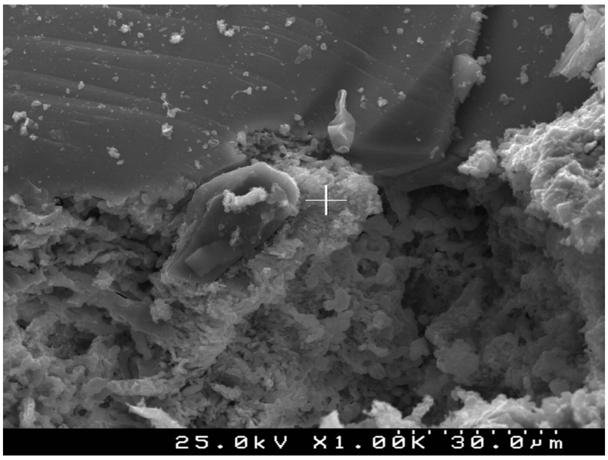


Fig. 5. Salts beneath the glaze of P133

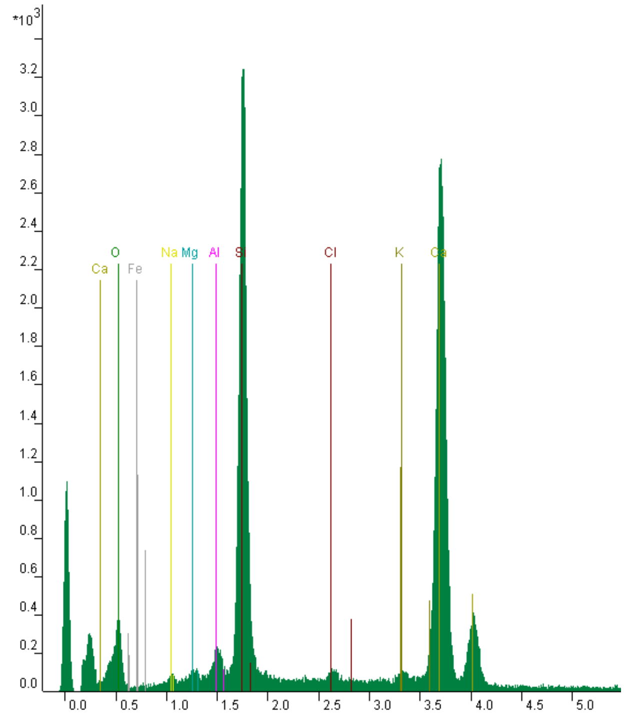


Fig. 6. EDS of the crystals marked in Figure 5

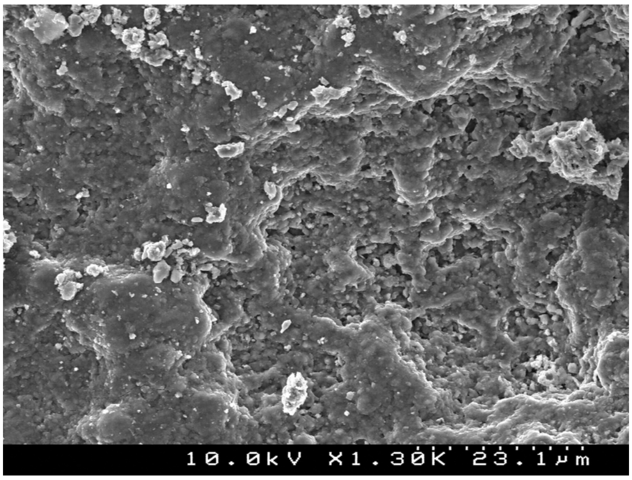


Fig. 7. A SEM view of the surface that suffered from glaze detachment

The studied samples, being already from the industrial era, have pressed ceramic bodies. Pressing gives to the ceramic surface a flat and even surface, one of the characteristic that distinguishes this producing era from the older ones. In Figure 7 it is shown a SEM view of the surface of the same tile used in Figure 4 (P133). It can be seen that the glaze detachment was made in depth, arriving at the ceramic body

Comparing Figure 4 and Figure 7 it is visible that the fracture propagation leading to glaze detachment due to salt attack is made under the interface glaze/ceramic body, probably meaning that interface thickness is not the most important characteristic to avoid the mentioned pathology. Probably the ceramic body porous system is the most important feature.

4. CONCLUSIONS

From the present study some observations can be already made about the complex subject of glaze detachment of 19th century tiles;

– When interface glaze/ceramic body is formed during firing, there is clear diffusion of potassium from the glaze to the interface, in most samples;

– The elements that seem more relevant in the interface composition are Si, Al, Na, Pb and K. Al, and Na show higher concentrations in the interface area than in the glaze or ceramic bodies. Al concentration in the glaze has an average value of 2.1 % and 8.8 % in the ceramic body, while in the interface it has 11.4 % as average value. Na presents an average glaze concentration of 0.5 % and 1.0 % as average value in the ceramic body, while the interface average value is 1.8 %.

– The presence of lead in the interface must be firing temperature dependant;

– Interface dimensions and composition of the studied samples are variable going from inexistent interfaces until 54 µm. Comparing the 54 µm value with the interface thickness of a contemporary tile (circa 18 µm), it can be concluded that the former has a rather big interface thickness. Even though, tiles with expressive interface thickness don´t resist to salt attack;

– It seems that even tiles with no measurable interface seem to hold time passing if, even in the exterior of buildings, placed far from the ground razing water panel place;

– In what concerns glaze detachment ability promoted by salt crystallization, volume and pore size of the ceramic body seems to be more determinant than glaze/ceramic body interface size.

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REFERENCES

1. **Flatt, R. J.** Salt Damage in Porous Materials: How High Supersaturation are Generated *Journal of Crystal Growth* 242 2002: pp. 435 – 454. http://dx.doi.org/10.1016/S0022-0248(02)01429-X
2. **Espinosa, R. M., Franke, L., Deckelmann, G.** Model for Mechanical Stress Due to the Salt Crystallization in Porous Materials *Constructioand Buildinn g Materials* 22 2008: pp. 1350 – 1367.
3. **Santos, T. P., Vaz, M. F., Pinto, M. L., Carvalho, A. P.** Porosity Characterization of Old Portuguese Ceramic Tiles *Construction and Building Materials* 28 2012: pp. 104 – 110. http://dx.doi.org/10.1016/j.conbuildmat.2011.08.004
4. **Scherer, G. W.** Crystallization in Pores *Cement and Concrete Research* 29 1999: pp. 1347 – 1358. http://dx.doi.org/10.1016/S0008-8846(99)00002-2
5. **Scherer, G. W.** Stress From Crystallization of Salts *Cement and Concrete Research* 34 2004: pp. 1613 – 1624. http://dx.doi.org/10.1016/j.cemconres.2003.12.034
6. **Cardell, C., Benavente, D., Rodriguez-Gordillo, J.** Weathering of Limestone Building Material by Mixed Sulfate Solutions. Characterization of Stone Microstructure, Reaction Products and Decay Forms *Materials Characterization* 59 2008: pp. 1371 – 1385. http://dx.doi.org/10.1016/j.matchar.2007.12.003
7. **Molera, J., Pradell, T., Salvadó, N., Vendrell-Saz, M.** Interactions Between Clay Bodies and Lead Glazes *Jounal of American Society* 84 2001: pp. 1120 – 1128.
8. **Molera, J. E. A.** Evidence of Tin Oxide Recrystallization in Opacified Lead Glazes *Journal American Ceramic Society* 82 1999: pp. 2871 – 2875.
9. **Kopar, T., Ducman, V.** Low-Vacuum SEM Analyses of Ceramic Tiles With Emphasis on Glaze Defects Characterisation *Materials Characterization* 58 2007: pp. 1133 – 1137.
10. **El-Defrawi, S. A., Serry, M. A., Weisweiler, W.** Microchemistry and Microstructure of Some Glaze/Tile Interface in Relation to Their Physical Properties *Ceramics International* 21 1995: pp. 69 – 75.
11. **Tite, M. S.** The Production Technology of Italian Maiolica: A Reassessment *Journal of Archaeological Science* 36 2009: pp. 2065 – 2080. http://dx.doi.org/10.1016/j.jas.2009.07.006
12. **Costa, M., Cachim, P., Velosa, A..** Glaze Detachment in Old Ceramic Wall Tiles – The Influence of Mortar Binder. Under Review. 2012.
13. I. P. Qualidade. EN ISO 10545-3. Determination of Water Absorption of Open Porosity. 2004.
14. **Smith, B. J., Warke, P. A., McGreevy, J. P., Kane, H. L.** Salt-Weathering Simulation Under Hot Desert Conditions: Agents of Enlightment or Perpetuators of Preconceptions? *Geomorphology* 67 2004: pp. 211 – 227. http://dx.doi.org/10.1016/j.geomorph.2004.03.015
15. **Cazalla, O., Rodriguez-Navarro, C., Cultrone, G.** Aging of Lime Putty: Effects on Traditional Lime Mortar Carbonation *Journal of American Ceramic Society* 83 2000: pp. 1070 – 1076. http://dx.doi.org/10.1111/j.1151-2916.2000.tb01332.x
16. **Cultrone, G., Sebastián, E., Rodriguez-Navarro, C.** Influence of Mineralogy and Firing Temperature on the Porosity of Bricks *Journal of European Ceramic Society* 24 2004: pp. 547 – 564.
17. **Molina, E., Cultrone, G., Sebastián, E., Alonso, F. J.** The Pore System of Sedimentary Rocks as a Key Factor in the Durability of Building Materials *Engineering Geology* 118 2011: pp. 110 – 121.
18. **Pereira, S. R. M., Mimoso, J.** Salt Degradation of Historic Portuguese Azulejos, Azulejar – Conservação de Revestimentos Azulejares em Fachadas, Universidade de Aveiro, Universidade de Aveiro – Portugal, 2012.
19. **Dias, T. C. D. G. E.** Salt Crystallization in Plastered or Rendered Walls. 2007.