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SALT DEGRADATION OF HISTORIC PORTUGUESE AZULEJOS

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SALT DEGRADATION OF HISTORIC PORTUGUESE AZULEJOS

Abstract

The glaze layer degradation of a set of Portuguese tiles from the XVII to the XVIII centuries has been researched. Within this study ageing tests were performed aimed at investigating a method for the simulation of *azulejos* physical decay.

The ageing due to the presence of NaCl salt and various conditions of drying temperature and water saturation have been imposed to the set of tiles that presented different characteristics and defects on their glaze layer. These defects were caused by previous degradation or production faults. The results showed that sample characteristics such as the porosity, vapor permeability and drying rate were decay drivers, but the existence of some particular glaze defects proved to be the most critical one.

DEGRADAÇÃO SALINA DE AZULEJOS HISTÓRICOS

Resumo

Este trabalho relata ensaios de degradação salina dos vidrados efetuados sobre um conjunto de azulejos portugueses dos séculos XVII e XVIII. Dentro deste estudo vários tipos de ciclos de envelhecimento foram executados de modo a investigar um método para a simulação da degradação física dos azulejos. O envelhecimento acelerado devido à presença de NaCl e várias condições de embibição/secagem foram assim impostas a um conjunto de azulejos com características diferentes e apresentando diversos defeitos de fabricação e/ou degradação prévia. Os resultados mostraram que propriedades dos azulejos como a porosidade, permeabilidade ao vapor e a velocidade de secagem promovem a degradação destes, no entanto foram alguns tipos de defeitos existentes no vidrado que demonstraram ser os maiores fomentadores da sua degradação.

SALT DEGRADATION OF HISTORIC PORTUGUESE AZULEJOS

Index

1. Introduction.....	1
2. Samples.....	3
3. Experimental.....	5
3.1. Samples preparation.....	5
3.2. Water imbibition-drying cycles.....	6
3.3. NaCl solution imbibition-drying cycles.....	6
3.4. Sample isolation during the drying cycles.....	7
3.5. Water vapor permeability.....	9
3.6. Monitoring of the degradation	9
4. Results and discussion.....	10
4.1. Ageing imbibition/drying cycles	10
4.1.1. Water imbibition coefficient and water capacity.....	10
4.1.2. Water vapor permeability	11
4.1.3. Influence of the back waterproofing method during drying	12
4.1.4. Drying Temperature.....	13
4.1.5. Water content (imbibition).....	16
4.1.6. Suggestions for the salt ageing protocol.....	17
4.2. Degradation by NaCl salt crystallization.....	18
4.2.1. Non-degraded samples without efflorescence (Samples A2 and A5).....	20
4.2.2. Non degraded samples with efflorescence (Samples A6a and A4).....	21
4.2.3. Efflorescence and glaze detachment (Sample A6b).....	22
4.2.4. Efflorescence and glaze degradation via detachment front (Sample A1).....	23
4.2.5. Glaze degraded around a pore (Sample A7).....	25
4.2.6. Glaze degradation via delaminated glaze detachment (Sample A3).....	26
5. Conclusions.....	28
Bibliographic references.....	30
Appendix A – Sample isolation methods.....	33

SALT DEGRADATION OF HISTORIC PORTUGUESE AZULEJOS

1. Introduction

From the possible forms of decay of Portuguese historical faience tiles, the most worrisome is the detachment of the glaze layer, because this contains the pigments and thus the image without which the artistic value of the tiles is lost. The detachment of the glaze layer involves the failure of the connection between the glaze and the ceramic body, but the reasons for this detachment are still not completely understood (Mimoso 2011). The loss of parts of the glaze layer can also accelerate the degradation by allowing moisture to enter into the ceramic body. The most frequently mentioned degradation causes are related to the presence of water: the presence of soluble salts and biologic activity, e.g. by lichens. Soluble salts are generally transported by water that migrates through the porous matrix of ceramic materials. The mechanisms of the damage caused by salts are considered to be the crystallization growth, hydration states, thermal expansion, and swelling of porous salt aggregates by moisture or temperature (Pique 2010). These crystallization characteristics are believed to induce mechanical stresses sufficient to overcome the ceramics mechanical strength and cause damage to the matrix (Angeli 2007) and to the glaze-ceramic body interface.

The damage caused by salts can become manifest in several ways besides glaze detachment such as glaze blistering, tile dampness, ceramic base disaggregation, tile fissuring and the less harmful salt efflorescence. The type of damage induced by the salt solution depends on the characteristics of the tiles, the type of salt that contaminates them, and the environmental conditions prevalent.

Sodium chloride is one of the most damaging and commonly encountered salts in Portuguese architectural heritage, primarily on areas located close to the sea (Nunes 2008). Whenever cyclic crystallization-dissolution occurs, strong crystallization pressures during crystal growth of sodium chloride can physically damage the ceramic materials by disrupting their porous matrix (Pique 2010).

The reason why, in the same conditions, some tiles decay while others do not is not yet completely understood. It seems, however, to be related to the occurrence

of susceptible areas in the tiles caused by (local) variations of their composition and/or physical properties. These heterogeneities could for instance have been caused by inhomogeneous raw materials, variations in the manufacturing procedure, or the result of actions suffered by the tiles during their existence. Decay is also favored by some manufacturing defects (Mimoso 2011).

Within this report we study the influence of NaCl salt degradation on a tile of the 17th and a group of tiles of the 18th centuries (Figure 1, Table 1) with different glaze defects such as delamination, pores, cracking and areas with lack of glaze (Table 2). An initial understanding of the behavior of the samples under imbibition/drying cycles was needed. For that purpose, several imbibition/drying conditions were tried, as well as the drying temperature and the amount of water imbibed in each cycle.

2. Samples

A tile of the 17th and a set of tiles of the 18th century (Figure 1, Table 1) in principle produced in the Lisbon workshops were selected due to the presence of distinct characteristics and glaze defects (Table 2).

All the tiles presented a blue and white majolica decoration and a more thoroughly physical-chemical characterization can be found at LNEC Report nr. 23/2011 (Pereira 2011).

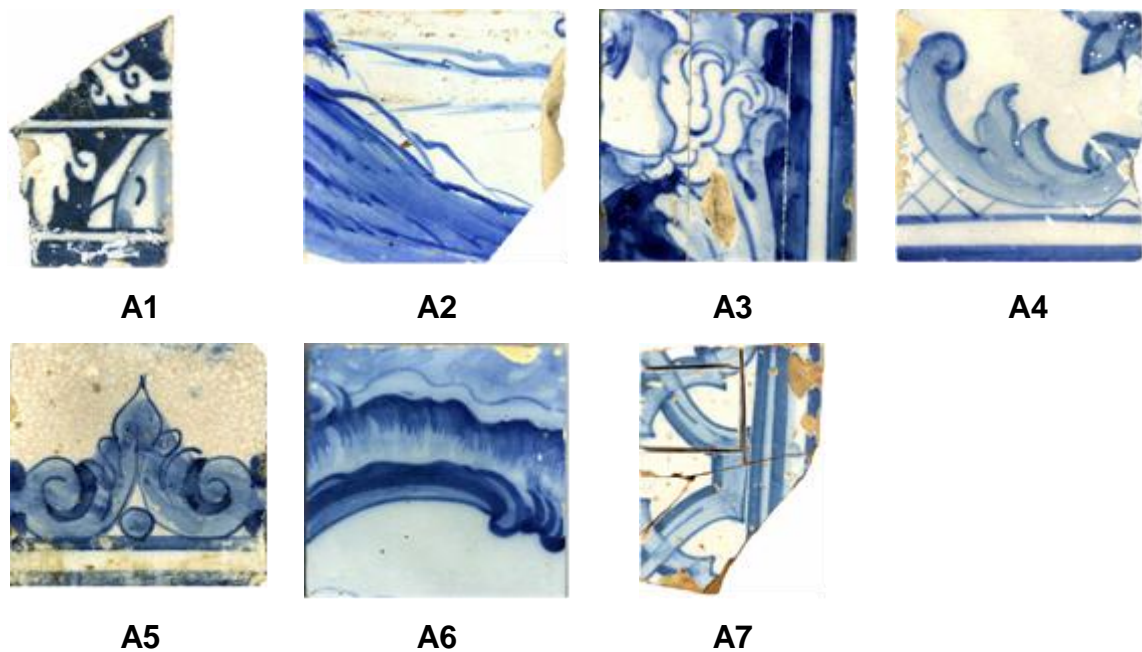


Figure 1. Ceramic tiles studied

Table 1. Historical Portuguese tiles tentative dating and observations.

Samples	Date	Observations
A1	17 th century	Sample buried for an unknown time. Cracked and delaminated glaze
A2	Early 18 th century	Loss of glaze along edge
A3	18 th century (1730-50's)	Delaminated tile
A4	18 th century (1760-80's)	Areas of glaze loss close to edge
A5	18 th century (1760-80's)	Cracked tile (craquelé). Possible organic contamination
A6	18 th century (1760-90's)	Loss of glaze along edge
A7	18 th century (1760-90's)	Several defects in the glaze layer

Table 2. Azulejo sample fragments (Section 3.1, Figure 2) characteristics and defects.

	Area (cm²)	Widht (mm)	Delamination	Pores (n)	Defects		Other
					Craquele	Exposed ceramic	
A1	40	15	Yes	4	Yes	No	-
A2	28	14	No	6	No	No	Saw incision on the edge, punctured
A3	31	13	Yes	1	No	No	Fissures in the glaze
A4	27	11	No	2	No	Yes	-
A5	18	11-12	No	0	Yes	No	-
A6a	22	11-12	No	2	No	No	-
A6b	6	11-12	No	0	No	Yes	-
A7	22	10	No	5	No	No	-

3. Experimental

3.1. Samples preparation

Fragments of the tiles (Figure 1) were cut (Figure 2) and their lateral sides isolated with a layer of epoxy resin to waterproof them and allow the water to be absorbed by capillarity only from the back. The top right corner without glaze of Sample A1 (Figure 2) was also covered with epoxy resin in order to promote the evaporation through the crack network of the tile. Artificial damage in the form of a saw incision (Figure 3a) and puncture (Figure 3b) have also been inflicted to sample A2.

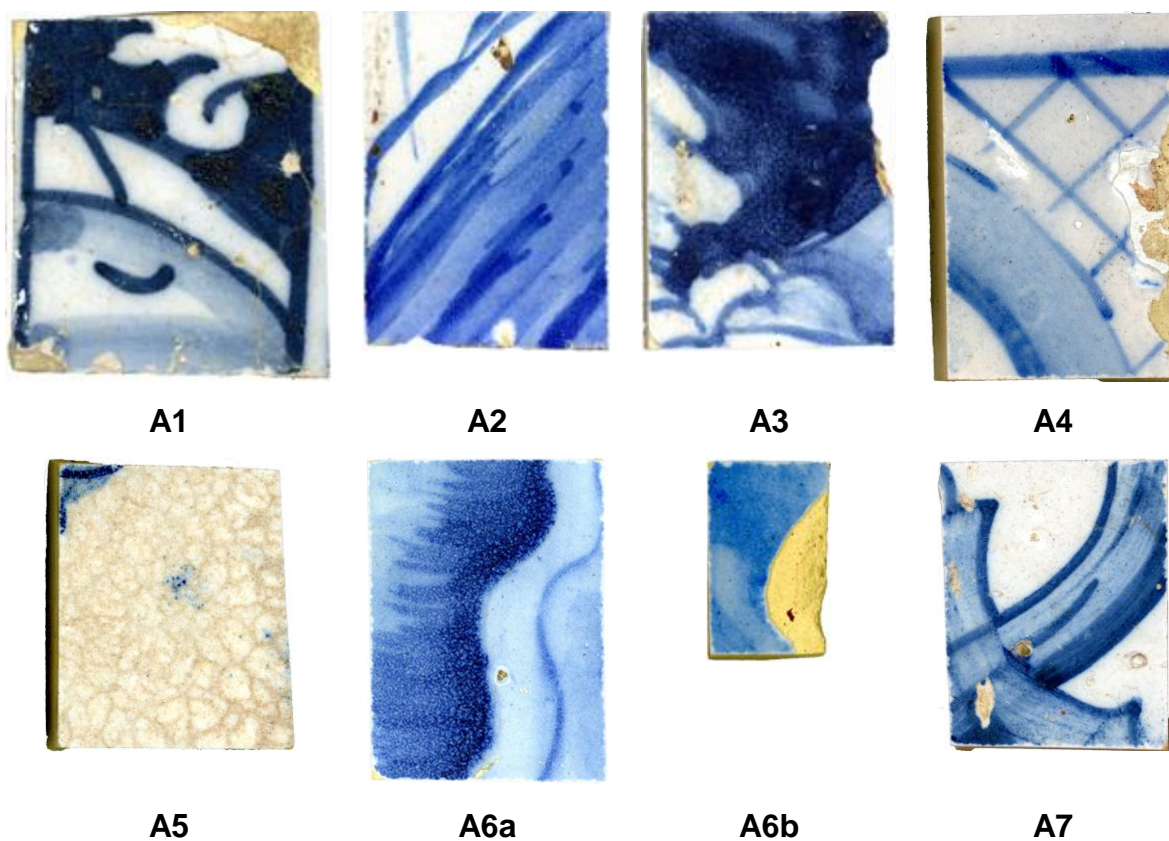


Figure 2. Azulejo fragments studied.

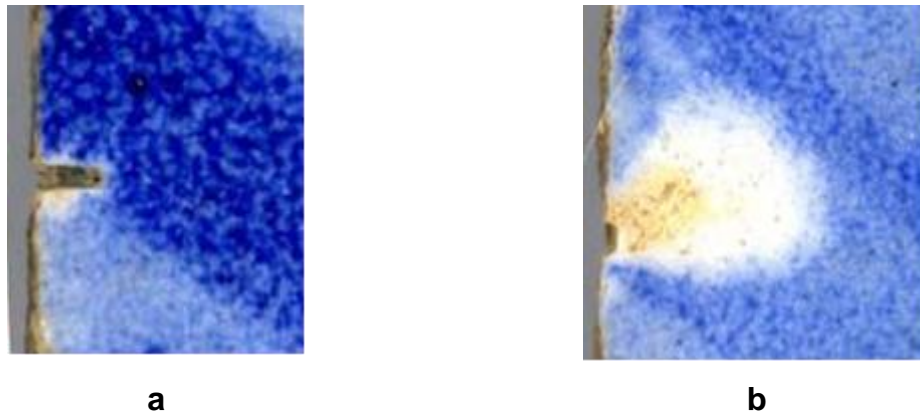


Figure 3. Artificial damage inflicted to tile A2. A) Saw cut, b) Puncture

3.2. Water imbibition-drying cycles

Before the imbibition cycles, the samples were dried at 60°C down to constant weight. For cycle Ci0 the samples were dried at 60°C for 12 h and then weighted. The samples were then positioned flat over a container with demineralized water and wetted up to about 0.5 cm of the tile width. The water absorption increment was monitored by periodic weighing of the samples. Afterwards the samples were let to dry at 60°C overnight.

3.3. NaCl imbibition-drying cycles

In the first crystallization cycle (Ci1) samples were imbibed with a solution of 300 g NaCl : 1 l demineralized water during 30 h. With their backs waterproofed (see 3.4), samples were then let to dry at 60°C in a ventilated oven until constant weight. In the second cycle samples were imbibed until saturation with demineralized water and dried in a ventilated oven at 60°C until dry. Table 3 indicates the imbibition drying cycles conditions to which the samples have been subject thereafter. Due to large differences in drying time, some samples have undergone a higher number of cycles (each sample went through at least four and up to 8 imbibition/drying cycles).

For the sake of experimenting, in some cycles the samples were imbibed with only half of their saturated value of water while in others all samples have been imbibed

for only 1 minute. Several drying temperature such as 40, 60 and 100°C have also been tried.

3.4. Sample waterproofing during the drying cycles

During the drying cycles several methods have been tested in order to prevent the evaporation through the back and enhance it via the front, around the glazed area. The several vapor proofing methods tried are illustrated in Appendix A. Method A1 comprised covering the back part of the tiles with a plastic film held by a rubber band (Appendix A, Figure 13). Method A2 used mastic to try to hold the plastic film on to the sample perimeter (Appendix A, Figure 14). Method A3 made use of an acetate layer in the shape of the back of the tile (Appendix A, Figure 15), attached with mastic on to the edges and covered with a final layer of thin plastic sheet. Method A4 was as A3 but using the high temperature resistant Sticky tape AT199 or AT200 from 3M instead of mastic (Appendix A, Figure 16).

Table 3. Imbibition-drying cycles conditions. D-dry, nD-not dry, S-saturated, d-days, m-minutes, h-hours.

Sample	Ci0	Ci1	Ci2	Ci3	Ci4	Ci5	Ci6	Ci7	Ci8
A1 Embib	Water -30h	NaCl-22h	Water- 22h S	Water-45m	Water-30m	Water-46h	Water-90h	Water-2m S	
A1 Drying	40°C-0.7d	40°C-13d 60°C-11d	60°C-32d D	60°C-9d D	60°C-20d nD	60°C-20d D	100°C-18d D	100°C-26d D	
A2 Embib	Water -30h	NaCl-22h	Water- 23h S	NaCl-30m	Water-90h	Water-2m			
A2 Drying	40°C-0.7d	40°C-13d 60°C-11d	60°C-54d nD	60°C-20dnD	100°C-18d D	100°C-26d D			
A3 Embib	Water -30h	NaCl-22h	Water- 22h S	NaCl-30m	Water-46h S				
A3 Drying	40°C-0.7d	40°C-13d 60°C-11d	60°C-54d nD	60°C-20d nD	60°C-20d D				
A4 Embib	Water -30h	NaCl-22h	Water- 7h S	Water-1h	Water-30m	Water-46h	Water-90h S	Water-2m	
A4 Drying	40°C-0.7d	40°C-13d 60°C-11d	60°C-37d D	60°C-9d D	60°C-20d nD	60°C-20d D	100°C-18d D	100°C-26d D	
A5 Embib	Water -30h	NaCl-22h	Water- 24h S	Water-27m	NaCl-30m	Water-46h	Water-90h	Water-2m	
A5 Drying	40°C-0.7d	40°C-13d 60°C-11d	60°C-18d D	60°C-36d D	60°C-7d nD	60°C-20d D	100°C-18d D	100°C-26d D	
A6a Embib	Water -30h	NaCl-22h	Water- 23h S	Water-15m	Water-5m	Water-30m	Water-46h	Water-90h	Water-2m
A6a Drying	40°C-0.7d	40°C-13d 60°C-11d	60°C-20d D	60°C-22d D	60°C-9d D	60°C-20d D	60°C-20d D	100°C-18d D	100°C-26d D
A6b Embib	Water -30h	NaCl-22h	Water- 23h S	Water-1.2m	Water-25m	Water-30m	Water-46h	Water-90h	Water-2m
A6b Drying	40°C-0.7d	40°C-13d 60°C-11d	60°C-20d D	60°C-20d D	60°C-9d D	60°C-20d D	60°C-20d D	100°C-18d D	100°C-26d D
A7 Embib	Water -30 h	NaCl-22h	Water- 22h S	NaCl-30m	Water-90h S	Water-2m			
A7 Drying	40°C-0.7d	40°C-13d 60°C-11d	60°C-54d nD	60°C-20d nD	100°C-18d D	100°C-26d D			

3.5. Water vapor permeability

The water vapor permeability has been measured after the salt ageing treatment of the samples (Section 3.3). On the lid of an impermeable plastic box an opening was made with the shape of the back of each sample minus one millimeter. The sample was laid on the top of the box and sealed with a 1:1 weight mixture of honey wax and golden pitch resin. The connection between the lid and the box was also sealed with this mixture (Figure 4a). The sealed samples were placed inside a box where NaCl brine maintained a relative humidity of about 75% (Figure 4b) and were time wise weighted for a period of 15 days.



a



b

Figure 4. Water vapor permeability. a) Sample A2 sealed, b) Vapor permeability chamber set-up.

3.6. Monitoring of the degradation

The alterations in the glaze layer have been monitored visually, by the use of optical microscopy and by the use of a 3D profile scanner Talysurf CLI 1000, with a spatial resolution of 50 μm .

4. Results and discussion

4.1. Ageing imbibition-drying cycles

4.1.1. Water Imbibition Coefficient and Capacity

The water absorption coefficient and imbibitions capacity (Figure 5, Table 4) are correlated to the pore structure of the materials and are indicative of the tiles fluids transfer characteristics. These characteristics can influence the degradation mechanisms of the porous materials such as *azulejos* and can be important parameters to assess their durability. As mentioned in the introduction water is considered the main cause of tiles degradation and the water flow characteristics and drying kinetics can govern the crystallization locations. Generally, the porous materials with a very slow capillary rise are less sensitive to decay since water is less prone to enter and circulate easily in the porous network. The porous materials with a quick capillary flow are usually more affected due to the ease of circulation and fast evaporation kinetics (Angeli 2007). In the case of glazed ceramic tiles however, since they are a composite material constituted by a porous ceramic layer and a less porous and largely impermeable glaze layer, the evaporation kinetics is highly dependant on the permeability and evaporation areas extant on its glaze layer. The crystallization is considered to be mainly governed by the evaporation kinetics allowed by the glaze layer and probably less by the capillary flow.

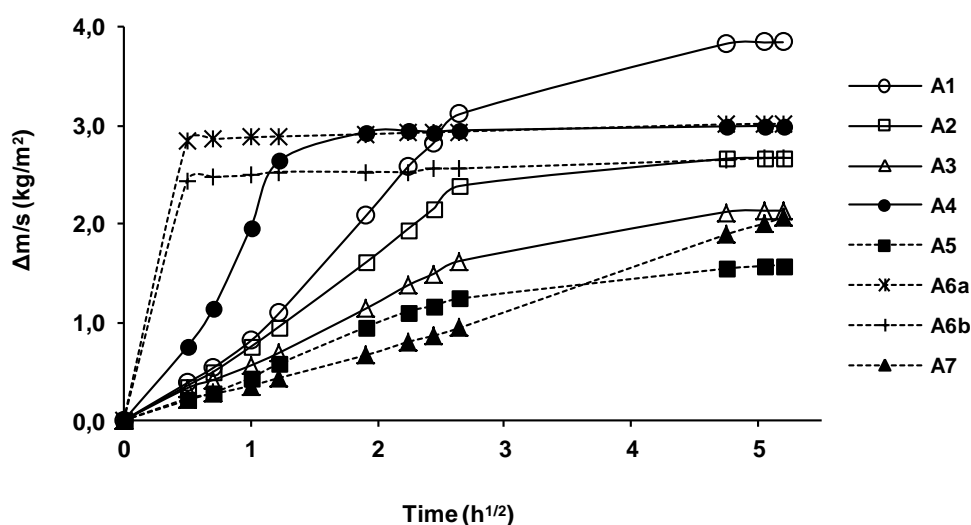


Figure 5. Ci0 capillary water absorption curves.

Table 4. CiO capillary water absorption coefficient.

Samples	Cap. Coef. (kg/m²/h^{1/2})	Imbibition capacity (% Wt)
A1	0.5	17
A2	0.4	12
A3	0.3	12
A4	1.2	17
A5	0.2	7
A6a	3.1	16
A6b	3.0	15
A7	0.2	12

Sample A6a and A6b followed by A4 are the samples with a higher capillarity coefficient. Sample A5 presents a low imbibition capacity due to fact that has been removed from a kitchen and is possibly impregnated with fat matter.

4.1.2. Water vapor permeability

The results of the water vapor permeability measurement (Figure 6 and Table 5) make evident the high level of impermeability of the glazed tiles except those that present relatively large unglazed areas such as sample A6b and A1. Sample A4 has, however, a large unglazed area but its permeability coefficient is relatively low. The unglazed area in this sample was caused, not by decay, but rather by the crawling of the glaze during firing. It has previously been noticed on sites that such cases do not depict the decay (e.g. sanding) that is expected on the unglazed areas even if exhibits decayed parts somewhere else on the surfaces. It may be hypothesized, as an explanation and a subject for future research, that notwithstanding the crawling, the raw glaze components have permeated the biscuit to the point of altering its permeability.

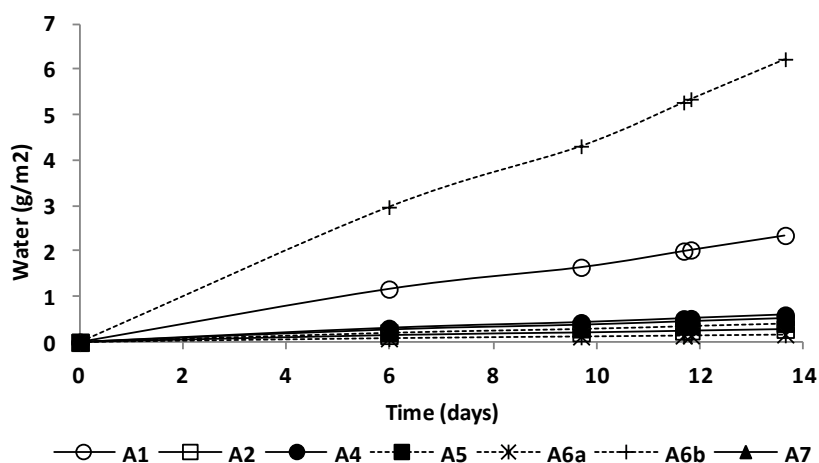


Figure 6. Water vapor permeability.

Table 5. Water vapor Permeability coefficients.

Sample	Perm. Coef. (g.m ⁻² .day ⁻¹)
A1	0,15
A2	0,02
A4	0,04
A5	0,03
A6a	0,01
A6b	0,42
A7	0,03

On the glazed ceramic tiles the glaze layer impermeability has an important role on the drying kinetics and therefore crystallization locations of the samples. The drying kinetics is dependant of numerous extrinsic parameters (relative humidity, temperature, air circulation, water content), of the porous networks characteristics (such as shape, size, connectivity, tortuosity) but also very dependent of the characteristics of the surface exposed to evaporation (Angeli 2007).

Due to the lack of permeability of the glaze layer, the time needed for drying the samples was found to be several orders of magnitude higher than that needed for the imbibitions, the drying time was undoubtedly the controlling factor of the imbibitions-drying cycles. During this study, the salt ageing cycles procedure has been modified several times in order to optimize and try to shorten the imbibition-drying cycles time. The parameters which have been modified were the isolation method, temperature during drying (40, 60 and 100°C) and initial percent of water content (saturation = 100%).

4.1.3. Influence of the waterproofing method during drying

In order to simulate the evaporation occurring on a tile in an architectural set-up where there is a water source from the back of the tile and the evaporation occurs close to the glaze layer there was the need to waterproof the back side of the tiles so as to drive the evaporation towards the glaze (see 2.4). The impermeability of the glaze and low height of the tile samples made the use of common waterproofing procedures inefficient. In this sense when using waterproofing methods A1 and A2, (Appendix A), it was observed strong crystallization on the back of the tiles indicating that the evaporation front was located on the back surface and not around the glaze layer. Waterproofing method A3 proved to be efficient at temperatures up to 60°C but not at 100°C due to the softening of the mastic and possible loss of some of its properties. Method A4 proved to be efficient also at 100°C because it can sustain higher working temperatures (maximum working temperature of 121°C and 204°C for sticky tapes AT199 or AT200 respectively).

4.1.4. Drying Temperature

The increase of the drying temperature allowed faster drying curves as can be seen in Figs 7-9 and Table 3.

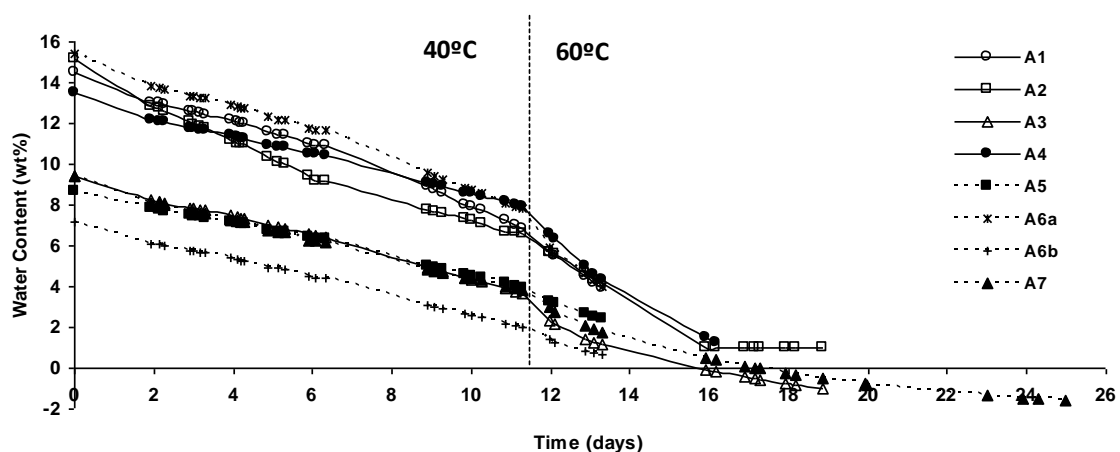


Figure 7. Drying cycle Ci1 where drying temperature was changed from 40 to 60°C.

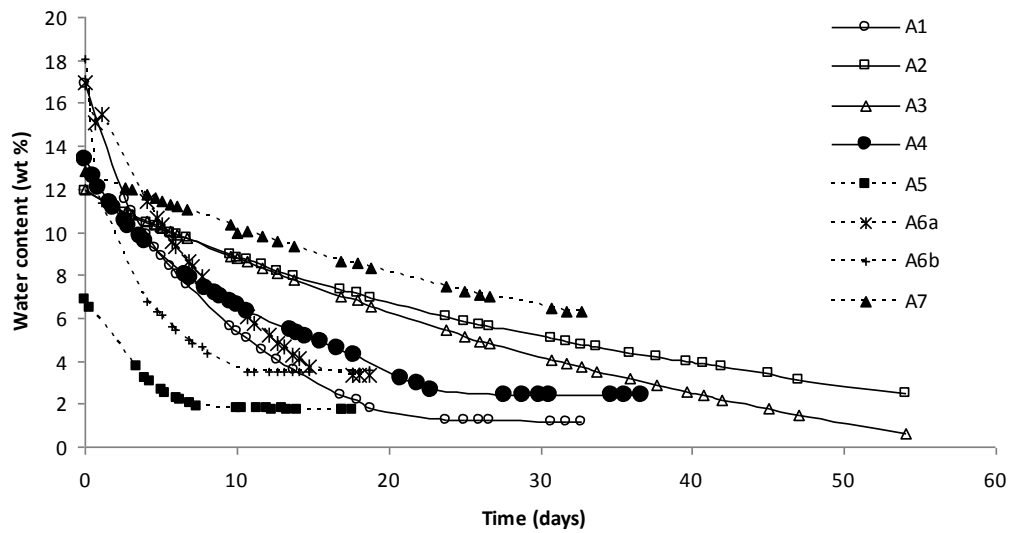


Figure 8. Drying cycle Ci2 at 60°C.

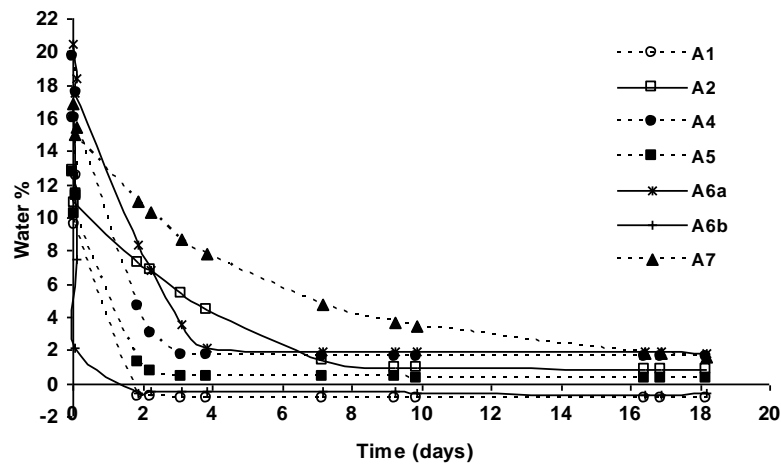


Figure 9. Drying cycle sample A2 and A7 Ci5, A1, A4 and A5 Ci7 and A6a and A6b Ci7 at 100°C.

Table 6 – Samples drying rate

Samples	Water Saturation (kg/m ²)	Drying time Days	
		60°C	100°C
A1	3.9	25	2
A2	2.7	> 54	10
A3	2.3	> 54	-
A4	3.2	28	3
A5	2.6	10	3
A6a	5.1	18	4
A6b	2.9	11	2
A7	2.8	>> 32	15

Note: water saturation indicated per unit area of glaze surface for comparison purposes

As expected, the drying temperature has an accelerating effect on the drying rate of the samples. While working with saturated samples and using sodium chloride, in order to be able to perform several cycles until total drying in a reasonable time span, a temperature of at least 60°C or preferably 100°C is recommendable.

The effect of the temperature on the degradation mechanisms of salt contaminated *azulejos* and its influence in the effectiveness of damage simulation could not be completely asserted from these results. A test campaign where several samples of the same tile would be subject to different drying temperatures would be necessary for a robust conclusion. We can only mention that the samples that exhibited efflorescence at 40°C (sample A1, A4 and A6b), also exhibited them at 60 and 100°C (Figure 10). This suggests that for these samples the capillary water supply was still faster than evaporation at any temperature allowing efflorescence to form at the surface.



A4- 60°C



A4- 100°C



A1-60°C



A1-100°C

Figure 10. A4 and A1 samples with efflorescence after drying at 60 and 100°C.

4.1.5. Water content (imbibition)

Decreasing the imbibition water content shortens the drying time needed, shortening also the total cycle time (Figure 11). With the current experimental set-up the effect on the drying and salt damage mechanisms could not be completely ascertained. Equal or similar individual samples subjected to repeated cycles each imbibed to different water contents would be necessary to observe the effect of this parameter. However, from the observations made, the samples imbibed with lower amounts of water and hence with lower water content did not show efflorescence after the drying cycles, indicating that the water supply to the evaporation areas was slower than the evaporation rate, leading probably to crystallization fronts inside the ceramic mass.

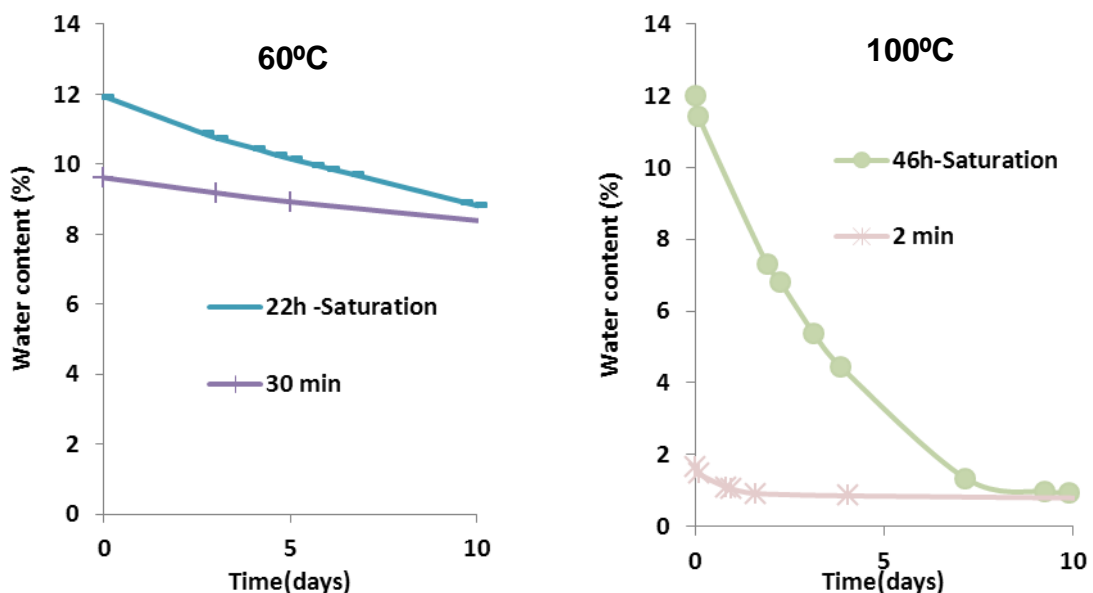


Figure 11. Drying curves of the A2 sample when imbibed for different time durations to obtain different water contents and dried at 60° and 100°C.

4.1.6. Suggestions for the salt ageing protocol

The lack of efflorescence observed when imbibing the samples with water below saturation is indicative of possible sub-efflorescence crystallization. With varying water contents at the imbibition step the drying front position is however difficult to control and may even be located deep into the ceramic matrix and not at the interface between the glaze and ceramic body layers. Imbibing the samples up to

saturation would therefore be advisable in order to better control the crystallization dynamics and increase the possibility of promoting crystallization close to the glaze-ceramic body interface. A possibility not tested under this work would be to saturate the sample and not wait for the completion of the drying cycle. In this way salts would crystallize close to the evaporation surface and crystallization deep inside the biscuit could be decreased augmenting the glaze degradation effects. The drying time is, timewise, the most important limiting step of the ageing procedure. In order to obtain faster cycles the drying temperature may be increased (up to 100°C). An efficient isolation is also important to mimic evaporation in an tiled damp wall and control the reproducibility of the drying cycles.

4.2. Degradation by salt crystallization

Two types of salt crystallization can occur in the samples: efflorescence and subflorescence. Efflorescences are salt crystals that have nucleated on the surface of the tile because salt solution supply by capillarity was faster than evaporation. They are therefore usually more massive on porous materials with a quick capillary flow and large evaporative areas. This effect could be seen on samples A4, A6b and A1. Efflorescences are usually largely harmless for the substrates and do not cause material damage but may account for aesthetical or dampness problems through deliquescence and can be again dissolved, even in air moisture, and then recrystallized as subflorescence (Nunes 2008).

When evaporation is faster than capillary flow, the salt solution does not have time to reach the surface before evaporating. The evaporation leads to crystallization of salts inside the porous network, possibly generating stresses that can be damaging to the ceramic matrix of the tiles (Flatt 2006, Angeli 2007). Subflorescences in opposite to efflorescences are therefore potentially more damaging. High porosities, low mechanical resistances and rapid kinetics of imbibition and evaporation are known to make the porous substrates more susceptible to damage by salts (Rodriguez-Navarro 1999, Angeli 2007). Salt precipitation inside a porous matrix can however also have a cementations effect,

damage may not arise straight away, however the hardened materials can exhibit a modified behavior under thermal or hydric dilation processes and can eventually detach. (Angeli 2007). Benavente et al says that porous materials, such as stone, with a high compression strength, Young's module or ultrasonic wave propagation velocities are believed to have a longer durability (Benavente 2006). This behavior is also expected for ceramic materials.

For stone materials some authors have demonstrated a good correlation between observed crystallization damage and porosity and pore size distribution (Angeli 2007). Due to diffusion, supersaturation of the salt solution is rapidly similar in pores of all sizes, the higher crystallization pressures should occur in the smallest pores. According to numerous studies, the porous materials that are the most susceptible to salt decay are those with the highest porosity and principally the highest proportion of small pores. (Angeli 2007) Porosity is directly related to the raw materials used (a high sand fraction and carbonates tend to originate extremely porous and permeable ceramics), and firing conditions such as temperature (when fired at high temperatures they are generally more vitreous and less porous) (Cultrone 2004). Thus the production method and raw materials determine the quality of the final product and, therefore, its susceptibility to the salt crystallization mechanism.

The location of salt precipitation both on and within a porous medium depends mainly on the salt solution supply, on evaporation areas and evaporation rates. Evaporation on glazed ceramics due to the high impermeability of the glaze will occur on the edges of the tile and other faults of the glaze such as pores, cracks, unglazed areas, etc. One of the purposes of this research was to study the influence that glaze defects have on the degradation of historical ceramic tiles.

The samples were thus chosen so that they presented several defects on their glaze layer (Table 2) . They also had different compositions and physical properties (Table 7). During the several imbibition-drying cycles (Table 2) the samples have therefore reacted differently to the degradation artificially induced.

Table 7. Physical and hydric properties of azulejo samples (Pereira 2011)

Samp.	MIP Porosity (%)	Pores mode (μm)	Spec. surf. area (m^2/g)	Imbibition capacity (% Wt)	Water Expansibility ϵ (mm/m)
A1	39	0.29 & 0.68	1.63	17	0.05
A2	34	0.04 & 0.46	3.68	12	0.42
A3	33	0.03& 0.45	3.96	12	0.33
A4	46	0.45	1.69	17	0.21
A5	32	0.7	3.91	7	0.26
A6	47	0.7	3.77	16	0.13
A7	36	0.02 & 0.065	12.66	12	0.30

Immediately after being fired the tiles absorb moisture from the air, expanding. The glaze which is not able to keep pace with the dimensional increase trend of the ceramic body is eventually put into traction until its limit tension is exceeded leading to crazing (Segadães 2003, Plešingerová 2002, Menezes 2006). Delamination could already be present as a result of manufacture due to lack of adhesion of the glaze layer to the ceramic body, or due to the glaze/ceramic fit (if the ceramic body contracts significantly more on cooling than the glaze and consequently a weakening of the interface or even a delamination by shivering may occur). The already delaminated tiles, or those with a weak glaze-body adhesion will be particularly susceptible to decay in the presence of water, with or without dissolved salts.

The degradation forms encountered during the salt ageing procedure will be discussed for the several samples.

4.2.1. Non-degraded samples without efflorescence (Samples A2 and A5)

Samples A2 and A5 did not present any visible signal of glaze layer deterioration after 5 and 7 cycles respectively (Figure 12). Efflorescence was not largely observed during any of the cycles.



Figure 12. Samples A2 and A5 after 5 and 7 cycles: a) A2 at final cycle Ci5; b) A5 at final cycle Ci7 and c) detail of unglazed area without efflorescence at A2.

The observation of lack of efflorescence on glaze uncovered areas of sample A2 indicates that the evaporation/crystallization could be located at a lower level inside the sample, below the glaze-biscuit interface on the ceramic matrix. The low glaze permeability (Table 5), low capillarity coefficient and relatively low porosity (Table 7) could justify the slow drying rate and longer durability of the samples. The low permeability of sample A5, despite its glaze craquelure structure could be explained because the tile was removed from a kitchen and is probably impregnated with fat organic matter.

The samples that did not have much exposed ceramic base areas through the loss of glaze were seemingly the less susceptible to physical degradation but the fact that they are not degraded to start with, may mean that they are particularly resistant to physical decay from the onset.

4.2.2. Non-degraded samples with efflorescence (Samples A6a and A4)

Sample A6a did not present any visible deterioration of its glaze layer and only a small efflorescence on a pore through the glaze (Figure 13). Sample A4 however, presented large efflorescence in all cycles except cycles Ci3 and Ci4 where saturation has not been reached during imbibition (Figure 14). No visible deterioration was observed in the sample except the loss of a white restoration mortar (Figure 12c).



Figure 13. Sample A6a: a) after 8 cycles and b) a detail of the efflorescence's in the glaze pore.

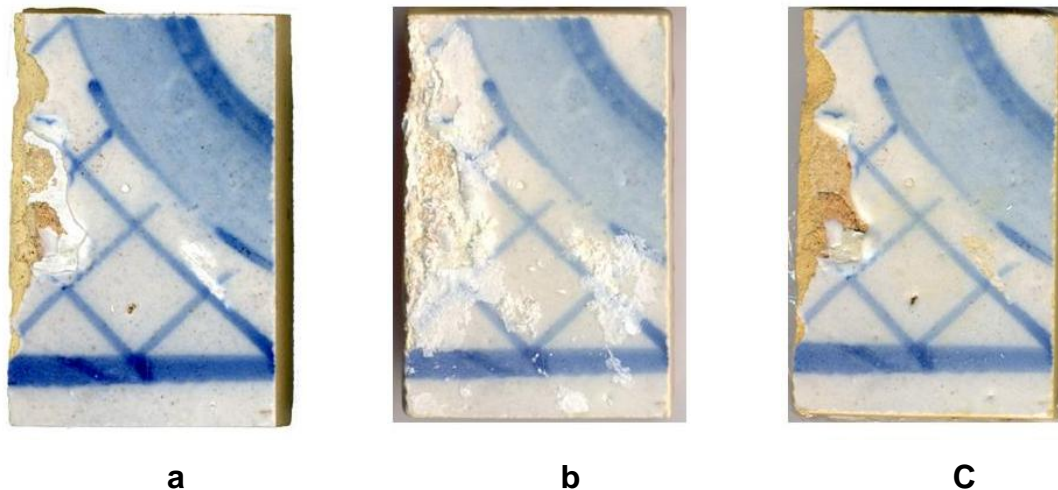


Figure 14. Sample A4 after cycles: a) Ci0; b) Ci1 and c) Ci4

Both sample A6a and A4 had a high capillarity coefficient and low permeability with medium drying rate. Together with the presence of unglazed evaporative areas this may have promoted the occurrence of efflorescence.

4.2.3. Efflorescence and glaze detachment (Sample A6b)

A6b has a high capillarity coefficient such as A6a, but due to its large unglazed area it exhibits high permeability and fast drying rate, the worst conditions when durability is considered. The reason this sample (A6b) from tile A6 dried faster than sample A6a is likely its large unglazed area but could also result from its smaller size.

Extensive efflorescence were observed and after cycle Ci5 a piece of the glaze detached. This sample was therefore more susceptible to degradation when compared to sample A6a.

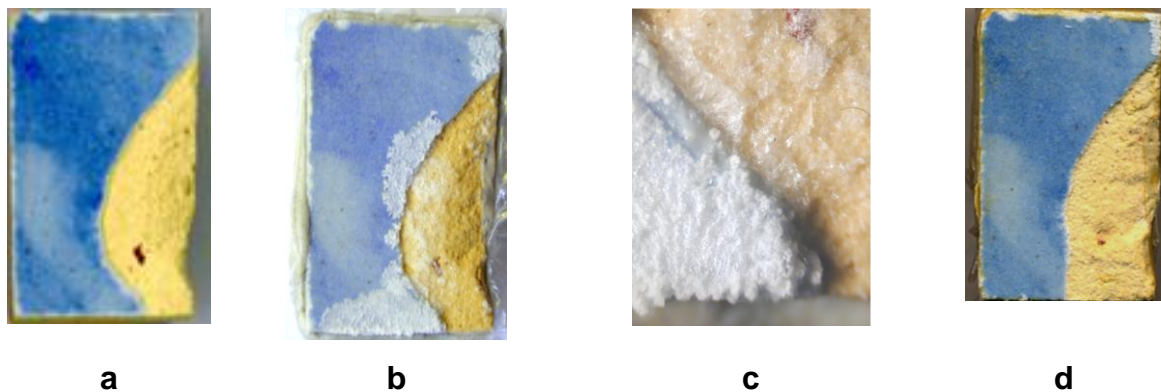
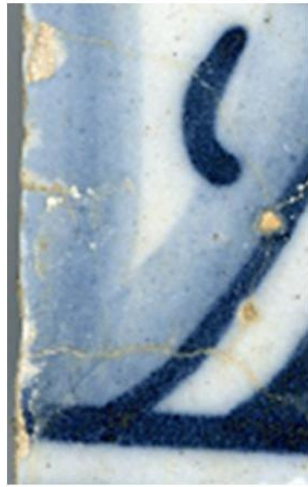


Figure 15. Sample A6b after cycles: a) Ci0; b) Ci1, c) detail Ci1, and c) Ci8

4.2.4. Efflorescence and glaze degradation via detachment front (Sample A1)

Sample A1 presents a moderate capillarity coefficient and drying rate but high permeability. The cracked structure of the glaze is probably responsible for its increased permeability. The fact that the sample presented Type II glaze fissures (interfacial propagation of crazing cracks – Mimoso 2011) proved highly sensitive to glaze damage under salt crystallization conditions. This resulted in consecutive detachments of the glaze layer on a so called “detachment front” (Figure 16 a-e). On the initial cycle it was observed that the efflorescence pattern spread relatively evenly through the surface and defects of the glaze (Figure 10). After some glaze pieces detached it was observed that the efflorescence concentrated on or closer to the unglazed area, an indication that the locus of salt crystallization is highly

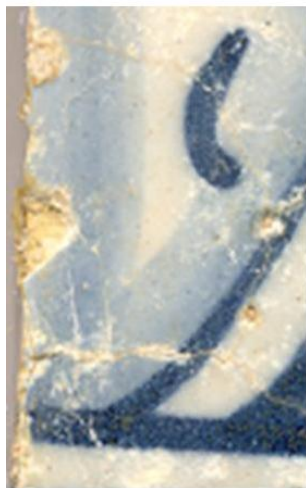
dependent of the asymmetries of evaporation rates and their correlation with capillary supply.



a



b



c



d

Figure 16. Detail of sample A1 glaze degradation after cycle: a) Ci0; b) Ci1; c) Ci3 and d) Ci4.

4.2.5. Glaze degraded around a pore (Sample A7)

Sample A7 presented very low capillary coefficient, low porosity with small pore size distribution, high specific surface area, and low drying rate. This sample would indicate to be less susceptible to decay except for the presence of small pore sizes and large specific surface area. However, even if not presenting massive degradation signals, after cycle Ci3 it started presenting some efflorescence and decay marks around a pore in its glaze layer (Figure 17). This sample had not shown any marks of degradation or efflorescence before this cycle. An influencing parameter could also have been the increase of salt content in its body through a second imbibition in saturated NaCl solution on this cycle. The slower drying rate of this sample was the reason for a lower number of cycles achieved (5 in the whole). After cycle Ci3, however, no new major deterioration has been observed.

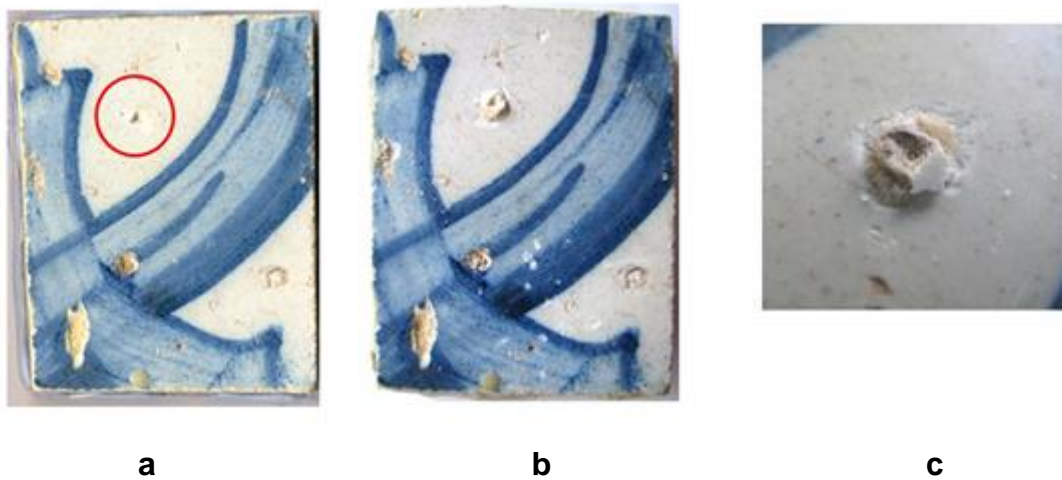


Figure 17. Sample A7 after cycles: a) Ci0; b) Ci3 and c) Detail of pore degradation.

4.2.6. Glaze degradation via delaminated glaze detachment (Sample A3)

Sample A3 presented a small capillarity coefficient, slow drying rate and we have no information about its permeability coefficient. Both these characteristics could indicate that it would be less prone to decay, however it turned out to be the sample with the most serious glaze degradation. In fact the delaminated area of the tile began to blister and crack (Figure 18) up to the point when, after few cycles, it broke off entirely, leaving a large unglazed area with remains of salt crystallization in the interface (Figure 19).

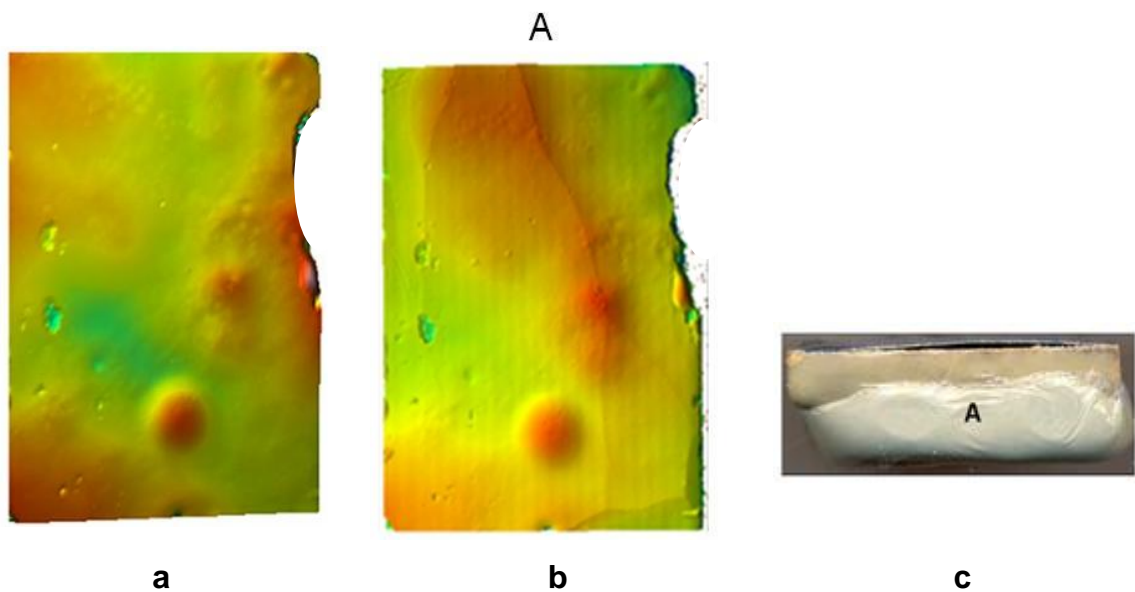


Figure 18. Surface analysis of sample A3 via a 3D profilometer with 20 μm resolution. a) Ci1, b) Ci2, c) lateral image of bulging glaze layer of sample at Ci2.

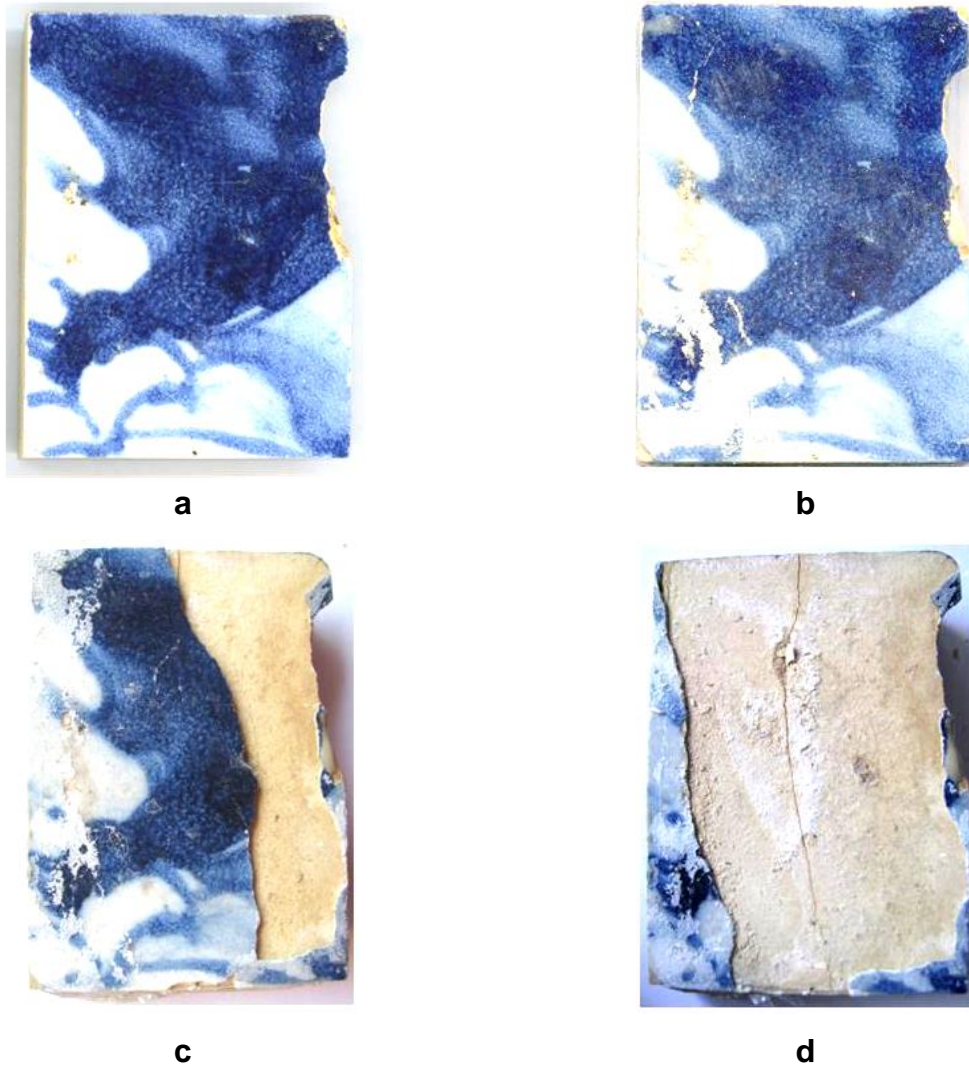


Figure 19. Sample A3 after cycles: a) Ci0; b) Ci2; c) Ci3 and d) Manual detachment of glaze after Ci3.

It could also be observed that the ceramic body was also fissured after the ageing cycles. This might be explained by the relatively high water expansion-contraction coefficient (Table 7) and the resulting stresses imposed to the biscuit (not homogeneous, showing coloured streaks and small round and elongated pores where stresses may concentrate) during the imbibitions/drying cycles.

5. Conclusions

The porosity, permeability and drying rate characteristics of the samples largely influence their water circulation behaviour and hence salt crystallization kinetics and so also degradation. However the occurrence of defects on the glaze layer that provide evaporative surfaces, have a large influence on tiles decay. The presence of defects such as glaze delamination and crazing with Type II fissures propagating in the glaze-biscuit interface proved to be the most serious decay fomenters.

The use of increased drying temperature largely reduces the time-limiting drying step. While not a realistic environmental temperature, 100°C decreased the drying time from months down to a couple of days in most samples, with no observable adverse consequences on the setting and propagation of decay.

Good vapor tightness of the samples sides is essential for a correct simulation of on site drying. While a great methodological improvement in the drying phase has been achieved through the control of the waterproofing, the method still presents some unreliability mainly at increased temperatures, when the vapor pressure is higher.

The effect of the use of imbibition with less water than that called for saturation would need to be tested and compared with sample fractions from the same tiles where saturated imbibition had been used.

The fact that the cracked-delaminated (A1) and the delaminated (A3) tiles were the most affected by the ageing cycles suggests that they were inherently fragile to this sort of challenge.

On the other side, great importance is attached to the fact that some of the samples did not show any damage whatsoever. Sample A2 has been intentionally damaged by blistering the glaze at the edge with a steel saw; however no decay was observed around the exposed biscuit. Sample A5, retrieved from a kitchen oven enclosure, had crazing cracks that seemed to be clogged by a greasy substance. The sample took the less water of all and did not show any efflorescence or damage whatsoever, suggesting that its biscuit porosity may be

partially occupied by foreign matter that hinders the uptake of water and its evaporation at the crack openings.

The onset of artificially induced decay offers important clues to the decay of *azulejos* onsite, but the fact that some samples seem impervious to the same challenges that degraded others offers also an important field of reflection. They provide clues to the frailties that are, so to say, built into the tiles by the manufacturing process or due to actions during the tiles existence and promote or hinder decay. These clues will be explored in the future.

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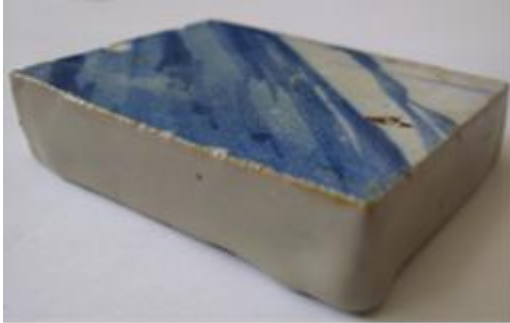
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Appendix A – Sample isolation methods

Four isolation methods have been tested and are described in Figures 13 to 16.

Isolation method A1



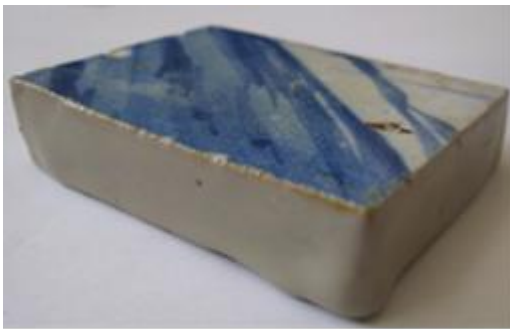
a



b

Figure 13. Vapor insulation method A1 of sample A2 using plastic sheet and an elastic. (a) with epoxy resin on the sides; b) With mastic and a plastic sheet after the drying cycle, with massive efflorescence's on the back. .

Isolation method A2



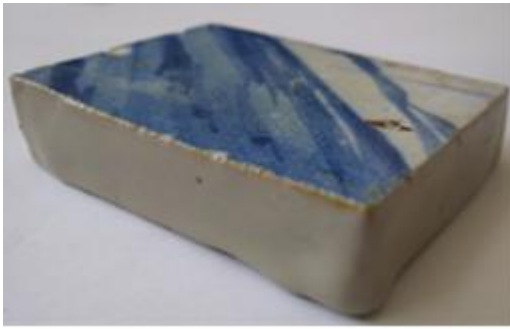
a



b

Figure 14. Vapor insulation method A2 of sample A2 using plastic sheet and mastic. (a) with epoxy resin on the sides; b) With mastic and a plastic sheet after the drying cycle, with efflorescences on the back. .

Isolation method A3



a



b



c



d



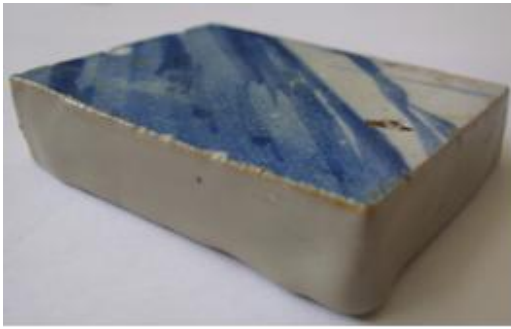
e



f

Figure 15. Vapor insulation of sample A2 using Mastic. (a) with epoxy resin on the sides; b) adding a rigid plastic sheet on the back; c) sealing with Mastic; d) Adding a plastic sheet in the end; e) final isolation view from the front; and, f) final isolation view with no efflorescences on the back.

Isolation method A4



a



b



c



d



e



f

Figure 16. Vapor insulation of sample A2 using Sticky tape AT199 from 3M. (a) with epoxy resin on the sides; b) adding a rigid plastic sheet on the back; c) sealing with Sticky tape AT199; d) Adding a plastic sheet in the end; e) final isolation view from the front; and, f) final isolation view with no efflorescences on the back.

Lisboa e LNEC, dezembro de 2011

VISTOS

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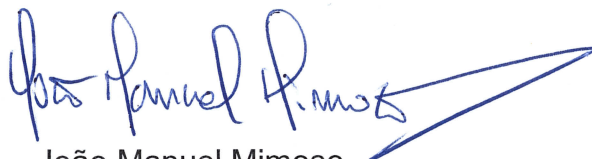


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