

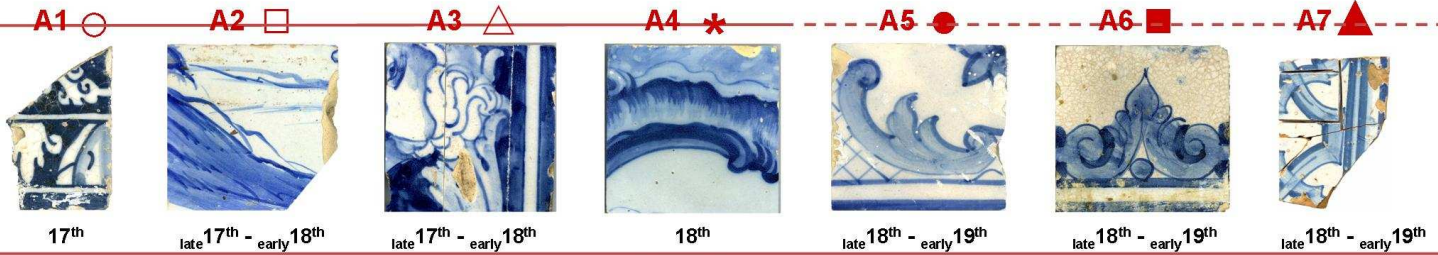
Physical-Chemical Characterization of Historical Portuguese Tiles (production and decay)

Silvia R. M. Pereira^a, Susana Coentro^b, António Santos-Silva^c, V. Solange F. Muralha^b, João-Manuel Mimoso^a

^a Laboratório Nacional de Engenharia Civil, Departamento de Materiais, Núcleo de Materiais Pétreos e Cerâmicos, Avenida do Brasil 101, 1700-066 Lisboa, Portugal, spereira@nec.pt, jmimoso@nec.pt
^b Research Center Vicarte, Faculdade de Ciência e Tecnologia, Universidade Nova de Lisboa, Monte da Caparica, 2829-516 Caparica, Portugal, scoentro@fct.unl.pt, solange@fct.unl.pt
^c Laboratório Nacional de Engenharia Civil, Departamento de Materiais, Núcleo de Materiais Metálicos, Avenida do Brasil 101, 1700-066 Lisboa, Portugal, ssilva@nec.pt

ABSTRACT

Portuguese historical tiles (*Azulejos*) are one of the most important assets of Portuguese cultural heritage. This rich heritage is being lost everyday by neglect and decay. The knowledge of the physical-chemical properties of the tiles is essential for its better knowledge, awareness and choice of proper conservation and restoration measurements. For those reasons a set of historical Portuguese tiles from the 17 to 19th centuries, believed to be from Lisbon production, have been physically and chemically characterized via multiple analytical techniques.

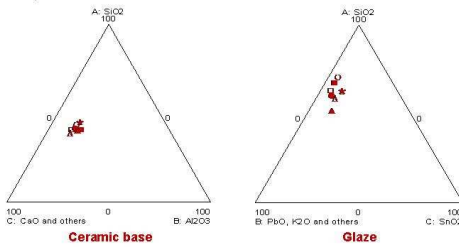


Chemical - Mineralogical

μ-EDXRF

The ceramic bodies elemental analysis resulted in similar compositions for all the tiles: 39-44 SiO₂, 12-15 Al₂O₃, 5-6 Fe₂O₃ and 35-41 wt% CaO. In all samples a low refractory Carich clay pastes has been used.

The glaze compositions were more diverse presenting values from: 52-71 SiO₂, 15-31 PbO, 5-9% K₂O and 5-11% SnO₂. Several different raw materials and recipes have been used during the tiles production.



XRD

The mineralogical composition of the ceramic bodies is more diverse than its elemental one. The raw material used could therefore have different mineralogical forms, granulometry and/or the firing conditions.

Mineral	Quartz	Cristobalite	Calcite	Gehlenite	Wollastonite	K/Na-Feldspars	Hematite	Analcime
Chem. F.	SiO ₂	SiO ₂	CaCO ₃	Ca ₃ Al ₂ (SiO ₄) ₂	CaSiO ₃	KAlSi ₃ O ₈	Fe ₂ O ₃	NaAlSi ₃ O ₈ ·H ₂ O
A1	++++	+	++	++++	Tr	++	Tr+	+++
A2	+++	Tr	++	++	+	+	Tr	Tr
A3	++	-	++	++++	Tr+	+	Tr+	-
A4	++++	-	-	++	++++	+	+	Tr+
A5	++++	-	+++	++	++	+	Tr+	-
A6	+++	Tr	+	++	++	+	Tr+	+
A7	++++	-	+++	++	++	+++	Tr+	Tr

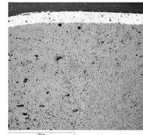
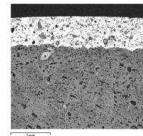
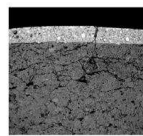
Semi-quantitative analysis: +++ high, ++ medium, + low, "Tr" traces and "-" not detected

TGA-DTA

A decrease in calcite content is observed for more recent tiles this could be caused by higher firing temperatures, longer firing cycles and/or deposition and re-carbonation of calcite with time.

Samples	Calcite (wt %)	Ca _{calcite} /Ca _{total} (mol %)
A1	19	28
A2	25	36
A3	25	33
A4	1	2
A5	12	17
A6	3	5
A7	12	19

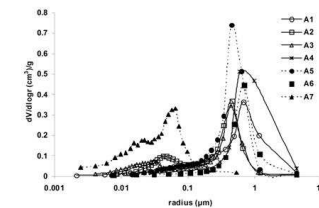
RESULTS



Physical

MIP and BET

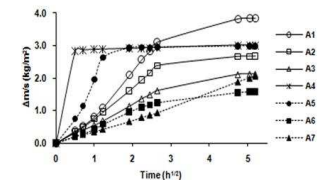
The pore volume and pore size distribution determine the capacity of fluids storage and ease of fluids circulation within the ceramic materials and are closely related to its degradation. Earlier tiles present a bimodal distribution. Samples with lower amount of calcite have a unimodal pore size distribution at 0.7 μm while high amounts sample have a bimodal character.



Samples	Porosity (%)	Pores mode (μm)	Spec. surf. area (m²/g)
A1	39	0.29 & 0.68	1.6
A2	34	0.04 & 0.46	3.7
A3	33	0.03 & 0.45	-
A4	47	0.7	3.8
A5	46	0.45	1.7
A6	32	0.7	3.9
A7	36	0.02 & 0.07	-

Capillary Water Absorption and Water Uptake

High open porosities and large pore sizes measured for A4 results in a higher water imbibition speed and maximum water uptake of the samples (A4 and A5).



Samples	Cap. Coef. (kg/m²/h ^{1/2})	Imbibition capacity (% Wt)	Maximum water uptake (mass %)
A1	1.2	17	22
A2	0.9	12	21
A3	0.6	12	23
A4	5.7	16	28
A5	2.1	17	26
A6	0.5	7	25
A7	0.4	12	23

Water and Thermal Expansibilities

Water expansion of ceramic materials is partially irreversible it starts after removal from the kiln and leads to increasing dimensions when the tiles age. It is a common cause of decay leading to crazing, detachment from the walls and glaze and ceramic bodies degradation. Sample A1 had been buried for undetermined time and showed the lowest expansibility. The coefficients of thermal expansion are similar in magnitude resulting in an expansion of about 0.2 mm/m for an increase of 25°C in temperature.

Sample	Water Expansibility ε (mm/m)	Coeff. thermal exp. (s) °C ⁻¹	dL/L (mm/m) (ΔT = 25°C)
A1	0.05	nd	nd
A2	0.42	6.9E-03	0.17
A3	0.33	7.1E-03	0.18
A4	0.13	7.9E-03	0.20
A5	0.21	6.6E-03	0.16
A6	0.26	6.8E-03	0.17
A7	0.30	6.9E-03	0.17

CONCLUSIONS

The similarity of elemental composition results points to use of similar raw materials and production techniques for the ceramic bodies but less so for the glaze. A decrease in ceramic base calcite content is observed during time indicating different producing procedures and tile properties with time. The different physical and chemical properties influence the dynamics of fluid flow, expansibilities and mechanical resistance of the tiles and hence its degradation mechanisms.

To understand the tiles degradation mechanisms and devise proper conservation and restoration measurements is essential to know its chemical-physical properties. A larger sample set is necessary to consolidate the results obtained and withdraw the main trends between the physical-chemical properties and the decay mechanisms of the tiles.

