Physical and chemical characterisation of ceramic wall tiles, dated to the 17th century, from the "Convento de Cristo", in Tomar, Portugal

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ABSTRACT Both the "monochromatic" (blue and white) and polychromatic (mainly blue, yellow and white) glazed ceramic wall tiles from the "Convento de Cristo", humanity heritage monument, located in Tomar (Portugal), are dated of the last decades of the 17th century. The physico-chemical characterization of the chamotte basis of those tiles, beige or light red coloured and around 1,5 cm thick, was carried out applying X-ray diffraction (XRD) and X-ray fluorescence (XRF) techniques. The ceramic wall tiles from the "Convento de Cristo" can be classified as calcitic faience, since their chemical analyses show that lime (CaO) is a major component, making around 17-34% of the tiles total mass. Lime, from clay composition, would have reacted with silica (SiO_2) and alumina (Al_2O_3) derived from the breakdown of clay minerals (hydrated aluminosilicates) forming the calcium aluminosilicate gehlenite ($Ca_2Al_2SiO_7$) and the calcium silicate wollastonite ($CaSiO_3$). The maximum firing temperature used in the manufacture of the ceramic tiles would have been around 1000ºC, since the major high temperature crystalline phases identified in the tiles were gehlenite and wollastonite, associated to minerals such as, quartz and K-feldspar. Mullite and hematite were identified as well as minor high temperature crystalline phases. Lead in contents within the range 642-2588 ppm was determined in the chamotte, meaning that for the glazing operation lead bearing raw materials without being submitted to previous thermal transformation were used. After being dissolved in water (lead is water soluble) they were directly applied onto the chamotte. Therefore, the glaze that coats the ceramic tiles belongs to the lead based type.

1. Historical introduction

"Convento de Cristo" is one of the most emblematic monuments of the town of Tomar that deserved the classification of Humanity Heritage by UNESCO. This monument shows diverse architectural styles and has been submitted along its history to several restoration interventions. The oldest building of the Convento de Cristo is the Charola, dated of the 12th century. Contemporary of D. Manuel I rule is the very elaborated portal existing at the south façade, as well as the Sala do Capítulo and its famous window. During D. João III (1521-1557) rule new cloisters, as well as the refectory and the dormitory belonging to the Ordem de Cristo, were built. During Filipes rule the main cloister was built, and during the D. João IV (1640-1656) and D. Afonso VI (1656-1683) rules most of the cloisters as well as of the corridors and chapels of the convent were faced with panels of ceramic wall tiles (azulejos) exhibiting styles and motifs proper of that epoch. The northern façade and the Frades Ward (1690) are contemporary of D. Pedro II (1683-1706) rule.

The studied ceramic wall tiles face the lateral walls of corridors, cloisters and chapels existing in the Convent. They exhibit monochromatic (blue) or polychromatic (mainly blue and yellow) patterns and are dated to the 17th century. At present most of them are not placed at the original sites. In fact, the studied specimens were sampled at the Convent warehouse, where a large number of tiles that have faced some of the Convent internal walls are stored. Inside the warehouse ceramic tiles collected in other monuments existing in the region of Tomar, are stored too. However, care was taken in order that the studied specimens would correspond to patterns largely represented at the Convento de Cristo.

The location of the studied specimens and their typologies classified by Simões (1997) are as follows: the monochromatic tiles are from Claustro do cemitério (Graveyard cloister) with reference CC-CT; from the Claustro da lavagem (Washing cloister) with reference CC-CL and classified as P-364; from the Corredor da administração (Administration corridor) bearing the reference CC-CA; from Escadaria Filipina (Filipin staircase) bearing the reference CC-EF and classified as P-67; from the Corredor do cruzeiro (Transept corridor) bearing the reference CC-CC and classified as P-407; the polychromatic tiles are from the chapel of Portocarreros and from the corridor leading to toilets and sacristy, bearing the reference CC-PC and classified as P-74; also, polychromatic tiles were collected at the warehouse bearing the reference CC-M2 and classified as C-34.

2. Analytical methodologies

Mineralogical analyses was performed by XRD, both in ceramic wall tiles using the powder technique, and directly on the glaze surface; the semiquantitative data was estimated following the Schultz and Thorez methods (Schultz, 1964; Thorez, 1976). Chemical analysis (for major, minor and trace chemical elements) of ceramic wall tiles was performed by X-ray Fluorescence (XRF). The chemical elements present on the glaze were determined using two analytical techniques: Atomic Absorption Spectroscopy (AAS) and X-ray Fluorescence (XRF) for semi-quantitative analysis of Co, Pb, Sb and Sn and Zn.

Chemical information concerned with glaze composition and the identification of high temperature phases present on the ceramic tiles, as well as the analysis of tiles microstructure, were carried out using a scanning electron microscope (SEM) equipped with an EDS X-ray spectrometer. Mechanical Resistance to Flexion was determined on the ceramic tiles using a Universal Mechanical Tests Machine, and Water Absorption Capacity was determined too.

3. Chemical, mineralogical and microstructural characterization of the glaze

The results of the chemical composition of the glaze show that silica (SiO_2) in contents higher than 40% and alumina (Al_2O_3) in contents around 6% are the glaze network formers. Lead (PbO_2) in contents higher than 20%, potassium (K_2O) in contents between 5-7% and sodium (Na_2O) in contents between 2-4% are the network modifiers, acting as flux agents. The opacifier is tin (cassiterite - SnO_2) that provides the white colour that makes the basis of the glaze, due to its high refractive index, small particle size, surface irregularity and low solubility in glazes (Tite, 1991). The colouring pigments are as follows: cobalt (CoO and Co_3O_4) that provides the blue colour; antimony (Sb) that provides, in association with lead (Pb) the yellow colour, also known as “Gialio di Napoli”, (Borgia et al., 2002); and iron (Fe_2O_3) that provides the brown colour. Traces of zinc (Zn) were found too.

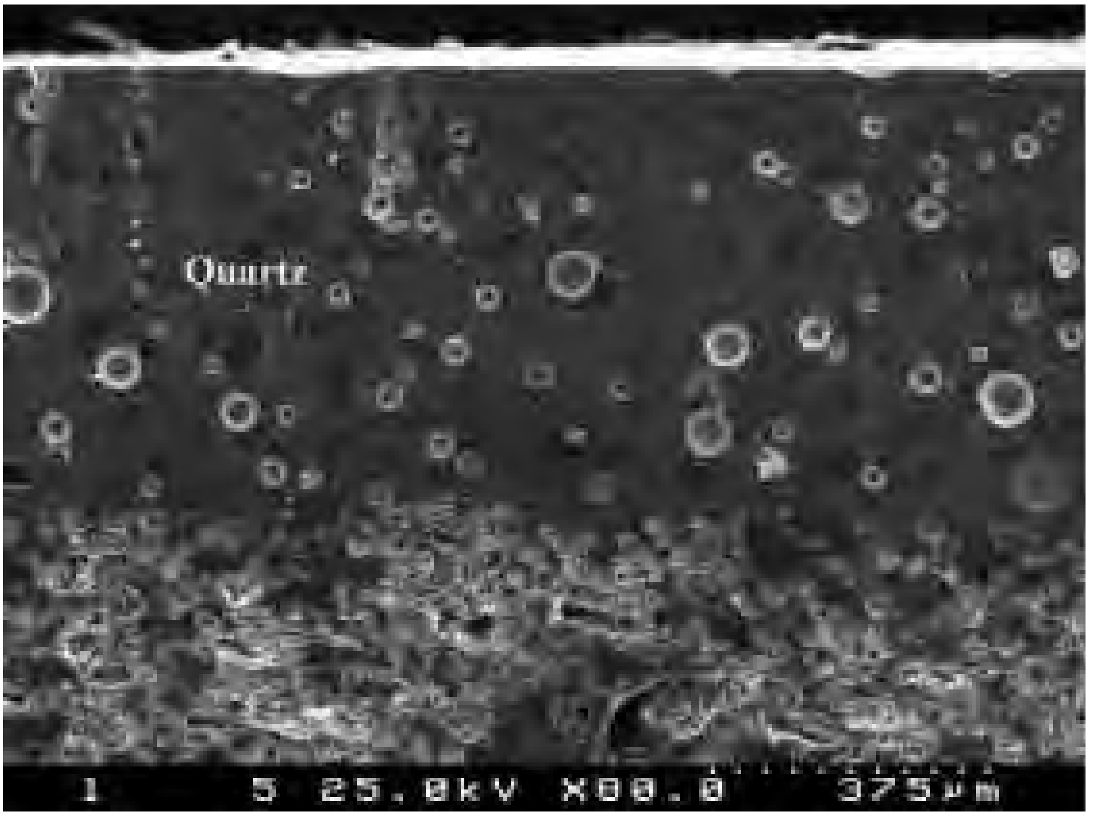

FIG. 1 – Quartz inclusions and bubbles inside the glaze; microstructural features of the glaze surface observed in CC-CC-1 sample.

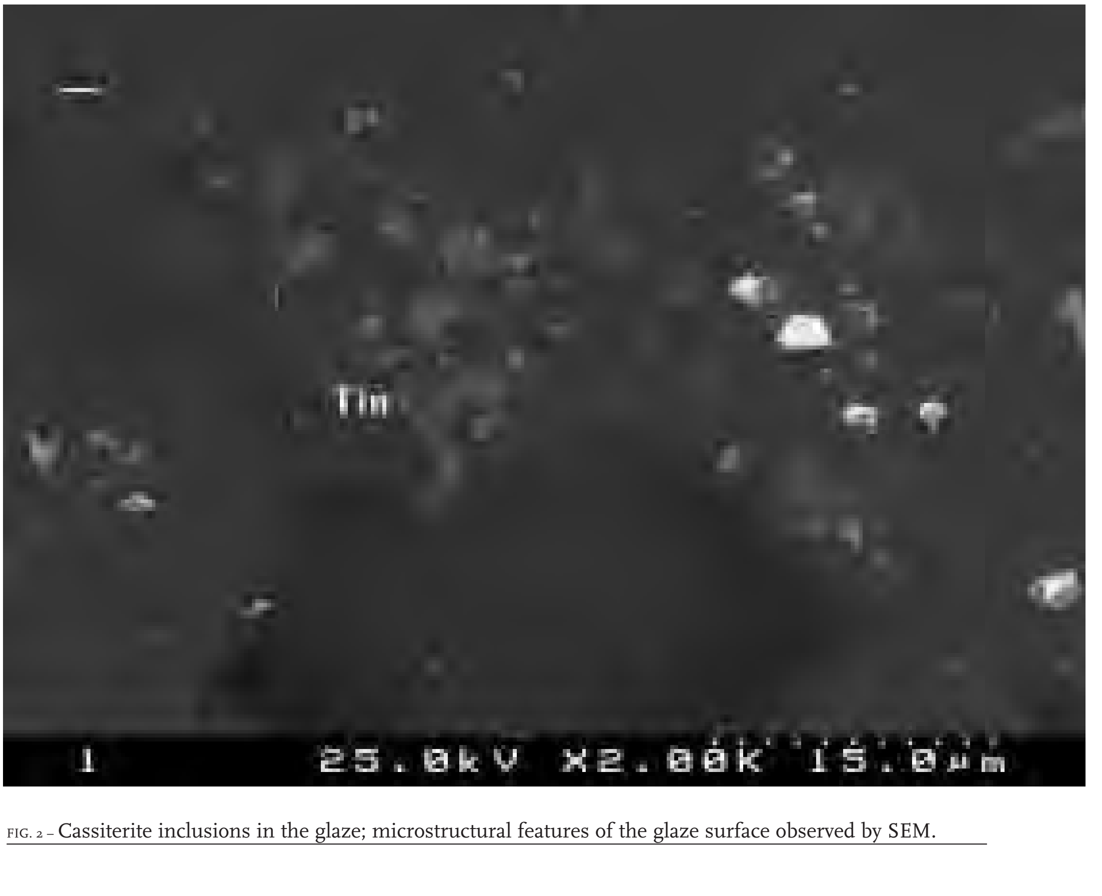

FIG. 2 – Cassiterite inclusions in the glaze; microstructural features of the glaze surface observed by SEM.

The mineralogical analysis carried out by XRD shows that the most abundant minerals are: quartz, SiO_2 (Fig. 1), cassiterite, SnO_2 (Fig. 2) and pyroclore, $Pb_2Sb_2O_6(O,OH)$. Talc, $Mg_3Si_2O_5(OH)_3$, cobalt oxides, CoO and Co_3O_4, and calcite, $CaCO_3$, were present too. In some specimens of the glaze alkaline feldspar was identified as well. Those minerals, and also the air bubbles (Fig. 1) act, as cassiterite, as opacifires which absorb, scatter or reflect light.

4. Chemical, mineralogical and physical characterization of the ceramic tiles

The chemical composition of the ceramic material determined by XRF show a composition typical of the calcitic faience (Table 1) (Gomes, 1990). In fact, CaO contents are within the range 17.64 – 34.33. To the highest CaO contents correspond to the lowest SiO_2, Al_2O_3, Na_2O, and K_2O contents. This fact points out to the utilization of distinct raw materials for the production of which group of tile.

Some tiles, CC-CT and CC-EF, show low CaO and MgO contents, and in such case the flux action was reinforced by higher Na_2O and K_2O contents. Intermediate compositions have been determined in some other tile specimens. In regard to the trace chemical elements (Table 2) the high Pb contents, within the range 642 to 2588 ppm, deserve particular mention, and apparently they aren't related with any other chemical elements; also, the relatively high Sr contents are directly related with CaO contents.

TABLE 1

Chemical data (major elements, in %), determined by XRF, on the ceramic basis of the tiles.

Samples	SiO_2	Al_2O_3	Fe_2O_3	MnO	TiO_2	CaO	MgO	K_2O	Na_2O	P_2O_5	L.o.I.
CC-CT-2	53,15	12,06	4,48	0,05	0,89	17,95	1,72	1,68	1,05	0,17	6,26
CC-CT-5	53,08	12,10	4,35	0,05	0,88	17,64	1,78	1,51	1,07	0,22	6,47
CC-CL-M1	45,98	12,03	4,58	0,04	0,30	21,05	2,89	2,71	0,58	0,15	3,14
CC-CL-1 14	45,87	10,90	4,35	0,05	0,91	25,92	2,13	2,03	0,84	0,22	6,05
CC-CA-1 26	38,22	9,75	4,18	0,05	0,88	31,87	3,02	1,53	0,63	0,20	9,05
CC-CA-2 23	35,98	8,47	3,72	0,04	0,84	34,33	4,45	0,94	0,47	0,20	10,19
CC-EF-1 20	53,48	13,14	4,90	0,05	0,95	20,01	2,02	2,75	0,91	0,24	1,08
CC-EF-2 17	51,43	12,87	5,08	0,06	1,00	21,49	2,15	2,82	0,73	0,22	1,33
CC-CC-6 8	48,96	12,03	4,80	0,04	0,90	24,78	2,95	2,48	0,84	0,20	1,64
CC-CC-P1	47,25	12,22	4,25	0,04	0,83	23,18	1,71	0,17	1,01	0,17	7,16
CC-CC-P2	41,41	11,41	3,68	0,03	0,80	27,70	1,84	0,18	0,73	0,18	10,30
CC-PC-1 11	44,49	11,21	4,55	0,04	0,92	23,39	2,31	2,37	0,93	0,18	8,66
CC-M2	37,06	9,87	3,76	0,04	0,73	30,88	1,81	1,63	0,86	0,15	13,04

TABLE 2
Chemical data (minor and trace elements, in ppm), determined by XRF, on the ceramic basis of the tiles.

Samples	Ba	Sn	Zr	Sr	Pb	Cu	Ni	Cr	V
CC-CT-2	240	12	147	196	1772	20	32	66	52
CC-CT-5	247	14	144	187	1832	20	32	76	50
CC-CL-M1	227	15	142	410	1261	14	26	61	48
CC-CL-1 14	160	16	124	304	2205	17	23	55	43
CC-CA-1 26	141	<5	106	371	1343	13	20	39	40
CC-CA-2 23	113	<5	105	459	989	16	19	33	37
CC-EF-1 20	272	<5	128	201	1378	16	31	67	50
CC-EF-2 17	243	6	128	206	1447	18	29	70	50
CC-CC-6 8	226	14	121	339	1764	20	25	65	47
CC-CC-P1	210	<5	103	256	3183	20	24	64	43
CC-CC-P2	151	<5	111	289	1938	15	21	38	42
CC-PC-1 11	197	26	128	315	642	16	25	56	49
CC-M2	147	<5	106	274	2588	16	19	45	41

FIG. 3 – Gehlenite identified in CC-CA-1 sample, after leaching the sample with a HF solution (1:1, during 60 s).

The mineralogical composition of the ceramic part of the wall tiles (Fig. 3) shows that quartz, gehlenite, wollastonite and diopside are the main components. Quartz is a residual component related to the raw materials, clay in particular, whereas gehlenite, wollastonite and diopside were formed from the reaction between CaO derived from the thermal decomposition of calcium or calcium and magnesium carbonate component from the clay raw material, and the silica-alumina glass that is formed after clay minerals dehydroxylation, this observations are consistent with other studies (González-García et al., 1990; Antunes et al., 1995; Lapuente and Pérez-Arantegui, 1999).

Other crystalline phases that occur in small or trace contents, such as mullite and a-cristobalite are also present. Illite/muscovite appears as a residual phase whose structure has not been fully collapsed during firing. The presence of calcite is the result of a recarbonatation process induced by solutions coming from the outside of the tile system and that percolate through it. This secondary phase can found cementing the pores or fissures.

The studied ceramic tiles show values of mechanical resistance to flexion (mrf) around 17 MPa, which are consistent with the values 12.0 MPa – 20.0 MPa of this property recorded on ceramic tiles of similar type. The highest values of water absorption correspond to the specimens with references CC-CA1 and CC-CA2 (25,7% and 22,9%, respectively) and CC-CC6 (23,4%). For the other specimens the mrf values are within the range 17,9%-14,1%.

In order to study the variation of the water absorption values as well as the variation of lead (Pb) contents on the ceramic part of wall tiles two test samples were collected, one from the ceramic tiles front and other from the ceramic tiles back, and the references CC-EF1, CC-CC-P1 and CC-Cl-1 were given to them (Table 4). The obtained results indicate that inside the ceramic matrix the water absorption values are similar, what means that tiles are homogeneous with regards to this property. Only for lead (Pb) the concentration in the back zone is higher than in the front zone.

TABLE 3

Mineralogical composition, determined by XRD, of the ceramic basis of the tiles.

Samples	Quartz	Gehlenite	Wollastonite	Diopside	Hematite	Calcite	Illite/moscov.	Others (tr.)
CC-CT-2	***	**	*	*	tr	tr	–	Mullite, a-crist.
CC-CT-5	***	**	*	*	tr	tr	–	Mullite, a-crist.
CC-CL-M1	***	***	*	*	*	tr	–	Mullite
CC-CL-1 14	***	***	*	*	*	tr	tr	Mullite, a-crist.
CC-CA-1 26	**	***	*	*	tr	–	–	–
CC-CA-2 23	**	***	*	*	tr	–	–	–
CC-EF-1 20	***	**	**	**	*	tr	tr	Felds.
CC-EF-2 17	***	**	*	*	tr	tr	tr	Mullite
CC-CC-6 8	***	***	*	**	tr	–	tr	a-crist.; feldsp.
CC-CC-P1	***	**	**	**	*	–	tr	a-cristob.
CC-CC-P2	***	**	**	**	*	–	tr	a-cristob.
CC-PC-1 11	**	***	*	**	*	tr	tr	Mullite
CC-M2	**	***	*	**	–	tr	–	–

*** – abundance (intensity or high structural order); * – rare occurrence; tr – trace occurrence

TABLE 4

Properties exhibited by the back zone and the front zone of the ceramic tiles.

Samples	zone	water absorption (%)	Pb (ppm)
CC-EF-1	Front1	17,4	965
	Back1	17,0	1553
CC-CC-P1	Front2	16,3	1108
	Back2	16,8	2287
CC-Cl-1	Front3	18,3	1291
	Back3	17,8	1408

5. Conclusions

5.1. Production model of the glaze

The glaze was produced using glaze raw materials, in aqueous suspension, and was applied directly onto the fired ceramic tile (biscuit), since we could observe incorporated into the glaze, either the presence of quartz and cassiterite grains, or differences in lead concentration between the front and back of ceramic tiles. Such, allow us to propose that lead migration and concentration at the tiles back, was favoured by the high porosity of the ceramic matrix, since both carbonate form of lead (cerussite, $PbCO_3$) and oxide form of lead (litharge, PbO) are soluble in water.

The concentration of cassiterite (SnO_2) near the interface between the ceramic body and the glaze, is due to the insolubility of this mineral in water. This finding confirms the utilization of glaze raw materials on the fired ceramic body. Such could explain the presence of bubbles produced during the degasification of the glaze.

The ceramic raw materials used on tile-making were mainly quartzose sand, clay of kaolinitic-illitic type, and a carbonate component, essentially calcitic, dispersed within them. The plastic conformation had been adopted for the ceramics shaping, and the firing temperature would had been around 1000°C. This ceramic processing model could be identified by the high water absorption values, and the good mechanical and chemical resistance values exhibited by the ceramic wall tiles, as well as by the high temperature phases, such as gehlenite, wollastonite and diopside, identified on them.

NOTES

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