IMPROVING THE KNOWLEGDE OF CERAMIC MATERIALS MANUFACTURE BY MEANS OF ANALYTICAL TECHNIQUES

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1. Introduction

Clay versatility is enhanced by the use of additives that enable the improvement of certain properties [1, 2]. Firing clays involves mineral phase changes that mainly depend on its composition, heating rate, maximum firing temperature, remaining firing time and oxidation or reduction kiln conditions [3, 4]. The firing temperatures reached can be deduced from the presence or absence of certain mineral parageneses [5]. Mineralogical variability is greater during firing in calcium-rich clay than low-calcium content clay [6].

Ceramic materials used at Former Workers Hospital of Maudes (Madrid, Spain), built between 1909 and 1916 by Antonio Palacios Ramilo (1874-1945), are studied. The building mainly consists of four bays arranged diagonally around several gardens, with a fountain in the central one. The brickwork walls comprise outer face stonework shaped mainly with limestone and some original staircases of the gardens are made of bricks. The building façades as well as the body of the fountain are decorated with ceramic pieces and the fountain basin is adorned with a tile *trencadiç*. At 80´s, nearly all the original ceramic pieces on façades were replaced and the fountain *trencadiç* was partially repaired [image 1]. Decorative ceramics used inside the building should be taken into account, as fountain tile *trencadiç* manufacture is probably connected with these materials.

References related to decorative ceramics [7-9] noted that original ceramic pieces were made by Daniel Zuloaga in Segovia (Spain) with iron oxide-rich red clay and silica added and were fired in an oxidising atmosphere at 1200 °C; that the original tiles for the basin fountain were pressed and manufactured by a Spanish Eastern or Sevillian (Spain) company; and that the interior decorative ceramics were processed by Ramos Rejano in Seville.

Such references also pointed out that at 80´s the replaced ceramic pieces of façades were mechanically pressed, using Madrilenian clay and sand from Segovia, grog from Teruel (Spain) and high quartz content as additives and they were fired under oxidising conditions at 1200-1250 °C; and that tiles used to repair the fountain tile *trencadiç* (made by extrusion) as well the inner decorative ceramics (by semi-mechanical pressing), were made from red mud, calcium-rich pastes and Madrilenian sand at Madrid's School of Ceramics and were fired at 1030 °C.

By means of optical microscopy and X ray diffraction analysis, bricks of inner walls and gardens staircases (both originals) and decorative ceramics (originals and made at 80´s) are studied. Findings of the analyses conducted are compared with the references consulted and new data on manufacture of ceramic materials found in a heritage building are provided.

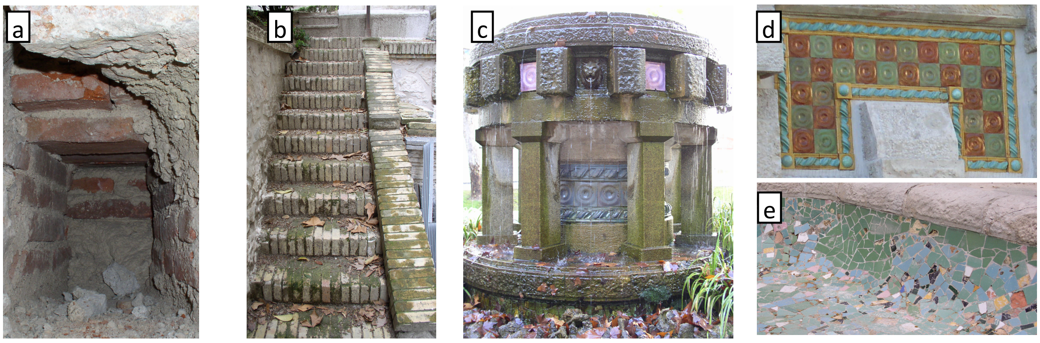

Image 1. Ceramic materials at Former Workers Hospital of Maudes (Madrid, Spain). Original bricks that shape inner fabric walls (a) and staircases of gardens (b); original ceramic pieces that decorate the body of the fountain (c); replaced decorative ceramic pieces on façades (d); tile *trencadiç*, original and repaired (upper area, with green color), that cover the fountain basin (e).

2. Results and discussion

2.1 Optical microscopy analysis

Image 2 displays polarized optical micrographs of the ceramic materials studied, where aggregate mainly comprised monocrystalline quartz grains.

The inner fabric wall bricks show significant chromatic and textural heterogeneity and high porosity, mainly due to its firing under uncontrolled atmospheres and its manual pressing, possibly at brickworks that were then located nearby the hospital [10]. The gardens bricks were carefully manufactured and the addition of generous amounts of grog, which enhance paste strength and avoid contraction during firing [2], can be observed.

Original ceramic pieces show grog and quartz aggregates with heterogeneous size as well as opaque minerals, possibly iron oxides from the red clay used [7], are observed. In both the original and replacement ceramic pieces, the important amount of quartz grains aggregates would confirm that silica was added to the original pastes and Segovian sand to the replaced material [7], mainly as a degreaser to improve the mechanical properties of the pastes [11].

The even texture observed in the replacement ceramic pieces, in terms of aggregate size and shape and of its orientation parallel or sub-parallel to the outer surface, was due primarily to the mechanised manufacturing procedure used [7]. In the original tiles, the aggregate: paste ratio is 1:3 and 3:1 in the repair material; this could point out that stronger pastes achieved by adding aggregate inclusions of quartz were employed at repaired tiles manufacture.

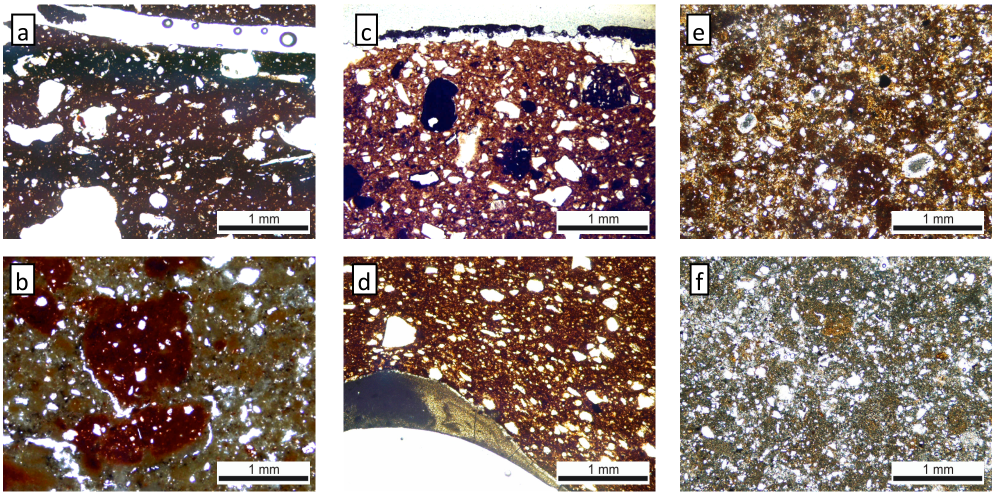

Image 2. Polarized optical micrographs of the ceramic materials studied (plane polarized light). Original bricks, from inner fabric walls (a) and staircases of gardens (b); original ceramic pieces that decorate the body of the fountain (c); replaced ceramic pieces on façades (d); original (e) and repaired (f) tile *trencadiç* that cover the fountain basin.

2.2 X ray diffraction analysis

Mineral phases identified by X ray diffraction are shown at image 3. At inner fabric walls bricks, the presence of hematites would reveal the existence of iron oxides in the clay raw material and/or they may have also been generated during firing [12]. The identification of gehlenite and anorthite would denote the use of a mix of kaolinitic and calcitic clays, in which, during the firing process, metakaolinite-gehlenite-anorthite recrystallisation would have taken place.

This reaction would have been enhanced by the structural similarity among these three mineral phases and expedited by the replacement of the aluminium in the kaolinite with iron [13]. The detection of gehlenite and anorthite would indicate that the temperature reached must have been over 950 °C. The high temperature mineral paragenesis identified in the gardens bricks (large amounts of wollastonite, diopside and anorthite and the near absence of gehlenite) reveals the use of a technology able to reach temperatures of over 1000 °C.

Firing temperatures reached for ceramic pieces, 1200 °C for originals [9] and 1200-1250 °C for replaced [7, 8] could not be confirmed. Nevertheless, since quartz concentration declines drastically from 1100 °C [14], the high quartz content ruled out firing temperatures of 1200 °C in the fraction analysed.

In the ceramic pastes used in gardens bricks and fountain original tiles, the absence of phyllosilicates and carbonates as well as the presence of wollastonite, gehlenite and diopside pointed out that the firing temperatures must have been higher than 900 °C and that the clay raw material had a high calcium and/or moderate magnesium content [6, 14]. This could denote that both ceramic materials could have been elaborated from the calcium-rich clay used at Sevillian traditional ceramic industry [15], so they could be manufactured by the same company (Ramos Rejano) that made the interior decorative ceramics. Besides, mineral phases identified at repair tiles pastes may confirm they were made with calcium-rich pastes and that the firing temperature was around 1030 °C [7]. The failure to identify anorthite and the presence of gehlenite and wollastonite in the repair tile pastes might be attributed to a low calcium or silica content in the clay used in their manufacture [9].

These high temperature (≈800-1000 °C) or neoformation mineral phases were generated in the clay paste during firing when the phyllosilicates in the clay raw material reacted with the calcium or magnesium oxide released during calcite or dolomite decomposition [16]. The presence of gehlenite and diopside together denotes firing temperatures of over 900 °C, while gehlenite alone is indicative of temperatures of over 800 °C and much higher than 900 °C if wollastonite is generated [16]. Diopside forms at higher temperatures than gehlenite and its presence entails the partial disappearance of the latter [15]. Gehlenite and wollastonite are regarded as intermediate compounds [17, 18] that became unstable phases in the presence of silica and high temperatures, generating neoformation phases with a higher silica content such as anorthite [6, 14, 16].

The intensity of the main diffraction peaks of the high temperature mineral phases may serve as grounds for establishing differences in the firing temperatures reached. The original tile pastes (Gh > Di, Wo and An) were therefore fired at a lower temperature (>800 °C) than the repair tile pastes (Gh ≈ Di and Wo; >>900 °C), which were in turn fired at lower temperatures than the gardens bricks (Gh < Di, Wo and An; >1000 °C).

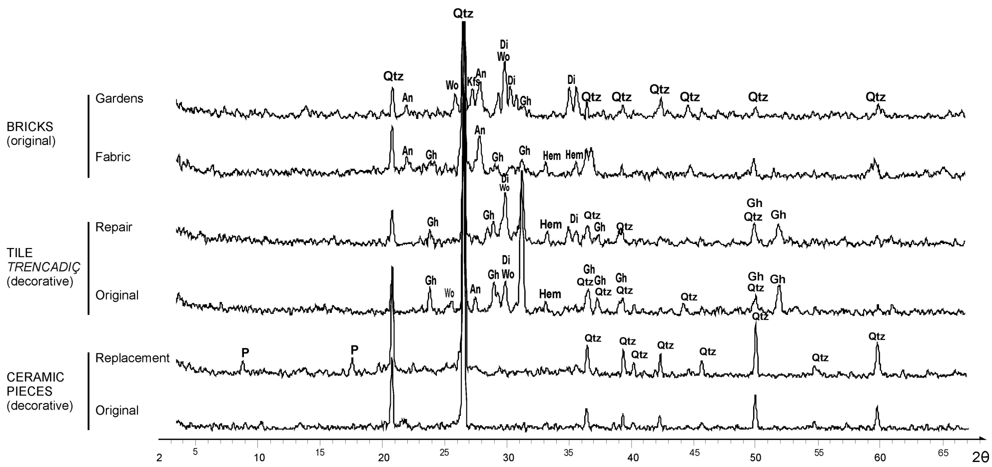

Image 3. Mineral phases identified by X ray diffraction on ceramic materials pastes (P: phylosilicates, Qtz: quartz, An: anorthite, Gh: gehlenite, Wo: wollastonite, Kfs: potassium feldspar, Di: diopside, Hem: hematite).

Conclusions

Inner fabric walls bricks and decorative ceramic pieces made by Zuloaga displayed uneven textural features, corresponding to their manual processing. Similar mineral parageneses identified at bricks from gardens and original tile *trencadiç* noted that they could be elaborated from related clay raw material and were probably manufactured by the Sevillian company that made the interior decorative ceramics. In order to increase the ceramic pastes strength, the manufacture of the materials studied carried out the use of grog and quartz aggregate inclusions as additives as well as firing temperatures circa 1000 ºC.

Acknowledgments

This research was funded by the Geomaterials (P2009/MAT_1629) and Geomaterials 2 (S2013/MIT_2914) Programmes and the Complutense University of Madrid's research group on the Alteration and conservation of heritage stone (921349).

References and recommended bibliography

[1] Kingery, W.D., Vandiever, P.M. (1986): Ceramic Masterpieces. Art, Structure and Technology. The Free Press, New York.

[2] Rice, P.M. (1987): Pottery analysis. A sourcebook. University of Chicago Press, Chicago.

[3] Maggetti, M. (1982): Phase analysis and its significance for technology and origin. In: *Archaeological Ceramics*, J.S. Olin (ed.), Smithsonian Institution Press, Boston, pp. 121-133.

[4] Maritan, L., Nodari, L., Mazzoli, C., Milano, A., Russo, U. (2006): Influence of firing conditions on ceramic products: Experimental study on clay rich in organic matter. *Applied Clay Science* 31, 1-15.

[5] Moropoulou, A., Bakolas, A., Bisbikou, K. (1995): Thermal analysis as a method of characterizing ancient ceramic technologies. *Thermochimica Acta* 2570, 743-753.

[6] Peters, T., Iberg, R. (1978): Mineralogical changes during firing of calcium-rich bricks clays. *American Ceramic Society Bulletin* 57(5), 503-509.

[7] Perla, A. (1990): La Cerámica. In: *Un Monumento recuperado: La rehabilitación del Hospital de Jornaleros de Maudes*, Consejería de Política Territorial, Comunidad de Madrid, pp. 131-161.

[8] Perla, A. (2001): Antonio Palacios y la cerámica: luz y color en la arquitectura. In: *Antonio Palacios, constructor de Madrid*, La Librería, Madrid, pp. 289-300.

[9] Rubio-Celada, A. (2004): De la tradición a la modernidad, los Zuloaga ceramistas. PhD Thesis, Universidad Complutense de Madrid.

[10] Checa, A. (1982): Evolución del plano de los barrios de Cuatro Caminos y Castillejos. *Anales de Geografía Universidad Complutense* 2, 167-180.

[11] Fazio, G., Hreglich, S., Lazzarini, L., Pirredda, L., Verita, M. (1982): Le Altinelle a Venezia: Problemi Storici, Caratterizzazione Chimico-Fisica, Cause di Deterioramento. In: *Il Mattone di Venezia. Contributi Presentati al Concorso di Idee Su Patologia, Diagnosi e Terapia del Mattone di Venezia*, Laboratorio Per lo Studio della Dinamica delle Grandi Masse, Venezia, pp. 227-291.

[12] Nodari, L., Marcuz, E., Maritan, L., Mazzoli, C., Russo, U. (2007): Hematite nucleation and growth in the firing of carbonate-rich clay for pottery production. *Journal of European Ceramic Society* 27, 4665-4673.

[13] Traoré, K., Kabre, T.S., Blanchart, P. (2003): Gehlenite and anorthite crystallisation from kaolinite and calcite mix. *Ceramic International* 29, 377-383.

[14] Trindade, M.J., Dias, M.I., Coroado, J., Rocha, F. (2009): Mineralogical transformations of calcareous rich clays with firing: A comparative study between calcite and dolomite rich clays from Algarve, Portugal. *Applied Clay Science* 42, 345-355.

[15] Flores, V., Guiraúm, A., Barrios, J. (1999): Caracterización de ladrillería tradicional producida en la Vega del Guadalquivir, en zonas próximas a Sevilla. *Boletín Sociedad Española Cerámica y Vidrio* 38(1), 29-34.

[16] Cultrone, G., Rodriguez-Navarro, C., Sebastian, E., Cazalla, O., de la Torre, M.J. (2001): Carbonate and silicate phase reactions during ceramic firing. *European Journal of Mineralogy* 13, 621-634.

[17] Riccardi, M.P., Messiga, B., Duminuco, P. (1999): An approach to the dynamics of clay firing. *Applied Clay Science* 15(3-4), 393-409.

[18] Traoré, K., Kabre, T.S., Blanchart, P. (2000): Low temperature sintering of a clay for pottery from Burkina Faso. *Applied Clay Science* 17(5), 279-292.