Applied Clay Science 163 (2018) 108–118

Contents lists available at ScienceDirect

Applied Clay Science

journal homepage: www.elsevier.com/locate/clay

Research paper

The use of mineralogical indicators for the assessment of firing temperature in fired-clay bodies

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ARTICLE INFO

Keywords:
Fired-clay bricks
X-ray diffraction analysis
Rietveld method
Firing temperature
Amorphous fraction

ABSTRACT

Fired-clay bricks are frequently object of conservative actions aimed at the preservation of cultural heritage. Information on firing conditions is relevant for the production of custom made replacement bricks, since, as a widely accepted principle, they should be close match to the pre-existing ones. In this work, the mineralogical and microstructural evolution of fired-clay bodies is described using a combination of analytical techniques, and an approach for the assessment of firing temperature using calibration curves built from the results of X-ray powder diffraction quantitative phase analysis with the Rietveld method, is presented. The weight fractions of hematite, mullite and the amorphous fraction, from two raw clays fired in the laboratory at different temperatures, have been used to assess the firing temperature of two industrially produced bricks. The values derived applying these three methods were in good agreement with the nominal temperatures of the industrial cycles. This approach might be of interest for the assessment of the firing conditions of a broader range of historical/archaeological fired-clay materials.

1. Introduction

The use of fired-clay bricks as construction material spread throughout Europe under the influence of the Romans. Although with geographical differences, it continued later, it flourished during the 19th century, and declined towards the second half of the 20th century.

Many brickworks have become objects of cultural heritage, and, because exposed for long time to a range of different environmental conditions, are nowadays raising various conservation issues (Baer and Livingstone, 2015; de Rojas et al., 2004; Maniatis et al., 1981; Schiavon et al., 2008). The conservation principles, established at national and international level, recommend the use of materials or techniques which are close matches for those being repaired or replaced, because they are recognised to carry a low risk of future harm or premature failure (Scolforo and Browne, 1996). For example, in case of stone objects, it is advisable, and sometimes possible, to use material from the same geological formation, or even the same quarry. The information about the source material is usually retrieved combining historical, archaeological and archaeometric data. For the replacement of fired-clay bricks, it would be required to gain knowledge of both the production process and the employed raw clay. Between the process variables, the maximum firing temperature has been considered of primary interest, because of its influence on the microstructure and, in turn, on the mechanical properties and the susceptibility of bricks to deterioration (Bauluz et al., 2004; Cultrone et al., 2004, 2005; Elert et al., 2003). In a recent study of historical bricks it has been proposed that the weight fraction of hematite and the unit-cell parameter of Mg-spinel might be used as indicators of firing temperature (Viani et al., 2016). This is in agreement with previous experimental evidences about the mineralogical, physical and chemical modifications occurring in clay bodies during thermal treatment (Cultrone et al., 2004; Khalfaoui and Hajjaji, 2009; McConville and Lee, 2005).

During firing of raw clays for brick production, sintering and recrystallization of the product of decomposition of clay minerals and development of new silicate phases, result in a new mineral assemblage and the formation of a fraction of glassy/amorphous phase. A substantial contribution to the amount of hematite detected in bricks comes from the iron initially present in the phyllosilicates of the raw clay (De Bonis et al., 2017), whereas Mg-spinel mostly forms as decomposition product of clinochlore (Barlow et al., 1997; Khalfaoui et al., 2006; Khalfaoui and Hajjaji, 2009), illite and kaolinite (McConville and Lee, 2005). Therefore, the firing conditions and the nature of the raw clay define the mineralogy and microstructure of the fired body (Cultrone et al., 2004). For example, relatively high spinel content (2.6–5.3 wt%) has been related to the chloritic nature of the clay feeding material (Viani et al., 2016). The unit-cell parameter of

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https://doi.org/10.1016/j.clay.2018.07.020
Received 21 May 2018; Received in revised form 11 July 2018; Accepted 13 July 2018
0169-1317/

spinel was considered a potential indicator of firing temperature, because essentially dependent upon the content in foreign ions, which increases with temperature, and less on the chemical composition of the raw clay.

The soundness of this, as well as of other methods, necessarily rests on an empirical basis, because of the complexity of the system and the process variables involved. It is therefore essential to extend the knowledge of the mineralogical and microstructural evolution of fired bodies to a larger number of raw clay materials. To this aim, and in order to contribute in the definition of a methodology based on mineralogical and/or microstructural parameters for the assessment of the firing conditions in fired-clay bricks, in this work raw clays from two brickyards of Czech Republic have been fired in a range of temperatures and dwell times. The raw clays and the fired products have been characterized with a combination of analytical techniques, and correlation curves for some mineralogical parameters, have been built. Results have been compared with those obtained from bricks fired in the production cycles of the two brickyards.

2. Materials and methods

In this study the raw clay and production bricks were collected from two localities in Czech Republic, namely, Štěrboholy and Sedlejov.

2.1. Site description and geological context

The brickyard located in Štěrboholy, now within the metropolitan area of Prague, started operation in 1927, but brick production in this area is much older. The original circular kiln has been substituted in 1992 with a tunnel kiln. Custom-sized bricks from this plant have been employed as replacement bricks for conservation works in Austro-Hungarian historical fortresses of the late 18th century, now located in Czech Republic, namely, Josefov and Terezin (Slavík et al., 2014). The raw clays are obtained from the nearby deposits. Nowadays, after excavation, they are homogenized and stockpiled at least for one year before use. Size reduction (< 5 mm) is followed by tempering and extrusion. The bricks are then dried at 80 °C for 6 days and later introduced in the kiln. According to the brick type, different firing cycles are in use. For the sample used in this study, the cycle comprised preheating at 140 °C, firing at nominal temperature between 950 °C and 1000 °C and cooling, lasting in complex 2 days.

The Štěrboholy area is part of Úvaly platform (part of bigger Říčany platform). The rock basement is formed mostly by Paleozoic rocks and relics of Mesozoic and Quaternary sediments (Chlupáč et al., 2002). The most common rock types are Paleozoic (upper Ordovician) dark grey/black, clay-rich and fine grained shales with organic content < 1% which contain some pyrite and gypsum. Other frequently represented rocks are fine grained siltstones (upper Ordovician) with calcite concretions. Other relics of the Ordovician strata are mostly black shales with higher organic content. The Quaternary sediments (Paleogene and Neogene), mostly of eluvial and fluvial origin, related to the erosion of the older rocks, are fine grained calcitic and clay-rich siltstones used as raw material in brick manufacturing (Kovanda et al., 2001).

The brickyard once located near the village of Sedlejov, few km from the historic town of Telč (Vysočina region), started production in 1922 and ended in 1972. It was equipped with a Hoffmann kiln with rooms for firing brick pallets in sequence, while maintaining the fire burning (Akinshipe and Kornelius, 2017). The excavated raw clay, was stockpiled before use and the extruded bricks were fired at temperature between 950 °C and 1000 °C (personal communication). Further details of the firing cycle were not available to the authors.

The geology of the Telč area is dominated by granitic rocks of the Moldanubicum massif (Luna, 2005). The latter is a Precambrian unit which underwent several metamorphic episodes. The rocks are mainly paragneiss and granites. Around Telč, the composition is rather homogeneous, consisting of small-to medium-grained mica monzogranites to granites with a predominance of quartz, potassium feldspar, plagioclase, biotite and muscovite. The superficial deposits are only tiny Neogene remnants and Quaternary products of weathering of the surrounding rocks. They include loess and loess loams, together with sandy and loamy fluvial sediments. The raw clays used in brick manufacturing were excavated from these Quaternary deposits. Geological maps at the scale 1:50000 of both areas are accessible through the website of the Czech Geological Survey (ČGS, 2018).

2.2. Materials

Dried extruded bricks from Štěrboholy brickyard have been used in the firing experiments conducted at the laboratory scale. 4 cm-edge cubes were cut from them before firing. In case of the brickyard of Sedlejov, since it no more exists, about 20 kg of raw clay were obtained from the original pit (coordinates: 50°04′49.9″N 14°32′41.6″E) several months after the material was exposed by an excavator. The raw clay was homogenized and reduced in size below 5 mm. The optimal conditions for laboratory screw extrusion through a die 4 × 4 cm resulted in 20.6 wt% of water added. 4 cm-edge cubes were obtained. The samples were kept in oven at 50 °C for 24 h and then at 80 °C for 24 h before firing. Firing was carried out in an electrical laboratory furnace under oxidizing conditions. The samples were preheated at 100 °C for 1 h and then brought to maximum temperature at heating rate 3 °C/min. Dwell times of 3 h were used. The samples were left to cool down by switching off the furnace. The following maximum firing temperatures were reached: 800 °C, 900 °C, 950 °C, 1000 °C, 1050 °C and 1100 °C. Additional dwell times of 5, 7 and 12 h at maximum firing temperature of 950 °C were also tested. One brick fired in the industrial cycle was collected from both sites. Samples were named using SE and ST for Sedlejov and Štěrboholy areas, respectively, followed by a number corresponding to the firing temperature in °C, or the letter B, to indicate the brick fired in the brickyard.

2.3. Analytical methods

Chemical analysis of the raw clays have been accomplished with X-ray fluorescence method using pressed pellets of finely ground samples dried at 110 °C overnight. Loss on ignition was measured after firing at 1100 °C.

The textural and microstructural features of the bricks were observed in thin section under a Carl Zeiss Jenapol-U polarized optical microscope (POM) equipped with digital photocamera. The sections were cut with orientation perpendicularly to the direction of extrusion. Investigations with field emission scanning electron microscope (FESEM) were performed on the same thin sections used for POM, but carbon coated. A Carl Zeiss SMT AURIGA instrument equipped with an energy dispersive detector AZTEC (Oxford Instruments) was used. The samples were coated with 5 nm thick gold film prior to analysis and observed at 20 kV accelerating voltage.

MIP analysis for pore-size distribution, bulk density, skeletal density and total porosity was conducted in triplicate on fragments cut from the central part of each sample. A Micrometrics AutoPore IV 9500 porosimeter, working at maximum pressure of 228 MPa, was employed. The covered range in pore diameter was 0.006–376 µm.

X-ray powder diffraction (XRPD) was performed for quantitative phase analysis (QPA) of both fired bodies and raw clays, previously dried at 110 °C overnight and then ground and homogenized by hand in agate mortar. Data were collected in the angular range 4–82° 2θ with virtual step scan of 0.0102° 2θ and 0.4 s/step counting time, by using Cu radiation at 40 kV and 40 mA. The Bragg–Brentano θ-θ diffractometer (Bruker D8 Advance pro) was equipped with a LynxEye 1-D silicon strip detector. Divergence 0.6 mm slit and 2.5° Soller slits were mounted on the incident beam pathway, whereas Ni filter, to select the K_α line (λ = 1.5418 Å), and Soller slits (2.5°) were mounted on the diffracted beam pathway. The samples were allowed to spin at 15 rpm