Applied Clay Science 166 (2018) 1–8

Contents lists available at ScienceDirect

Applied Clay Science

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

Research Paper

# Evolution of fine microstructure during firing of extruded clays: A small angle neutron scattering study

Alberto Viani[a,*], Radek Ševčík[a], Marie-Sousai Appavou[b], Aurel Radulescu[b]

[a] Institute of Theoretical and Applied Mechanics of the Czech Academy of Sciences, Centre of Excellence Telč, Batelovská 485, CZ- 58856 Telč, Czech Republic
[b] Forschungszentrum Jülich GmbH, Jülich Centre for Neutron Science JCNS, Aussenstelle am MLZ, Lichtenbergstraße 1, 85747 Garching, Germany

ARTICLE INFO

*Keywords:*
Fired-clays
Small angle neutron scattering
Extrusion
Anisotropy
Porosity

ABSTRACT

The microstructure of extruded fired-clay bodies in the interval 800–1100 °C has been investigated with small angle neutron scattering. The evolution of the retrieved pore size distribution is compatible with the coarsening of the pore network with increasing temperature. The analysis of the scattering curves in combination with results of electron microscopy, indicated a multiscale nature for the pore-matrix microstructure. A structural parameter obtained from the analysis of the scattering curves, is proposed as indicator of maximum firing temperature through the implementation of a linear calibration curve. Such method has been successfully tested on a material of industrial production and can be considered of interest for the production of custom made replacement materials in the conservation of cultural heritage or for the characterization of the manufacturing process of archaeological fired-clay objects. Textural features originated by the forming process of extrusion have been detected as anisotropy of the pore network. They are still present above 1000 °C and, because of the use of screw extrusion, they are observed in both sections cut parallel and perpendicular to the direction of extrusion.

## 1. Introduction

Fired-clay is one of the oldest construction materials and fired-clay bricks still find extensive use in the building industry nowadays. Compared to other construction materials (e.g. cement-based materials), much less efforts have been devoted to the elucidation of the relationships between microstructure and properties in order to optimize process variables and improve material performance. The microstructure of fired-clay bricks comprises a range in pore sizes from the subnanometric to the millimetric scale (Cultrone et al., 2004; Freyburg and Schwarz, 2007; Krakowiak et al., 2011; Viani et al., 2018; Viani et al., 2016a), which, similarly to other materials, such as cements (Winslow et al., 1995) and rocks (Anovitz and Cole, 2015), gives rise to a multiscale porous network. Therefore, the quality of the pore surface usually depends on the scale of measurement, and the specific surface area (governing interfacial phenomena, such as chemical reactions or diffusion) is largely contributed by the finest porosity (Barbera et al., 2013; Okolo et al., 2015). The complete coverage of the porosity in fired-clay bricks can be obtained only through the use of a multi-technique approach, also to overcome the inherent limitation of the available analytical methods (Busch et al., 2017; Cultrone et al., 2004; Krakowiak et al., 2011).

Bricks shaped with the extrusion technique exhibit anisotropy of physical properties (i.e. thermal conductivity, elastic properties), inherited from the processing steps and the preferential orientation of the clay mineral particles of the feeding material (Bartusch and Händle, 2009; Bourret et al., 2015; Habelitz et al., 2001; Krakowiak et al., 2011; Maillard and Aubert, 2014). As in other clay-based textured materials, such as mudrocks, shales (Busch et al., 2017; Gu et al., 2015; Jin et al., 2011) and ceramics (Antal et al., 2015; Boussois et al., 2013), the microstructure of extruded bricks is also characterized by orientation in the pore network (Bourret et al., 2015; Krakowiak et al., 2011), which originates anisotropy in water transport, with implications for material resistance to degradation (Krakowiak et al., 2011). The description of the pore network is relevant to the material performance, and for the understanding of processes such as brick deterioration (e.g. action of dissolved salts or moisture expansion) (Charola, 2000; Hansen and Kung, 1988).

Nowadays, many brickworks are considered part of cultural heritage and often need restoration (Baer and Livingstone, 2015; de Rojas et al., 2004; Schiavon et al., 2008). In compliance with modern conservation principles, brick replacement should be done in the least invasive way (Scolforo and Browne, 1996), therefore, ideally, adopting bricks produced from the same raw clay and employing the same

---

[*] Corresponding author.
*E-mail address:* viani@itam.cas.cz (A. Viani).

https://doi.org/10.1016/j.clay.2018.09.002
Received 17 July 2018; Received in revised form 29 August 2018; Accepted 4 September 2018
0169-1317/

production process. The maximum firing temperature has been considered the most relevant process variable, 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., 2005, 2004; Elert et al., 2003). It is therefore of interest to devise a method for inferring the maximum firing temperature in the event of brick replacement in historical buildings. Moreover, information on firing conditions is of relevance for the characterization of manufacturing processes in archaeological fired-clay bodies (Barone et al., 2011; Cultrone et al., 2005; De Rosa and Cultrone, 2014; Maniatis and Tite, 1981; Matsunaga and Nakai, 2004).

In this work we report on the microstructural characterization with small angle neutron scattering (SANS) of extruded clay bodies fired at temperatures from 800 to 1100 °C. Results will be compared with those obtained from an industrial brick produced from the same raw clay. Microstructural evolution and the role of anisotropy will be discussed in the light of the transformations taking place in the fired body.

## 2. Materials and methods

### 2.1. Raw materials and sample preparation

The clay raw material employed in this study has been collected from the site of the old brickyard near the village of Sedlejov, few km from the historic town of Telč (Czech Republic), a UNESCO World Heritage Site. The brickyard was in operation from 1922 to 1972, and the bricks have been used locally in masonry works. The clay was excavated and stockpiled before use; extruded bricks were dried in the chambers of a Hoffmann type kiln to be then fired to the maximum temperature of 950–1000 °C (J. Buzek, personal communication). Chemical analysis of the raw clay, obtained by X-ray fluorescence, is reported as Supplementary Material Table S1. About 20 Kg of the raw material 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 clay was dried, reduced in size below 5 mm and homogenized. Further homogenization was obtained by adding 20.6 wt % of water to reach good rheological properties for laboratory screw extrusion. The clay bodies were obtained by forcing the clay through a die with cross section 4 × 4 cm. The extruded body was cut to obtain cubes with edge 4 cm. Before firing, the green samples have been dried in oven at 50 °C for 24 h and then 80 °C for 24 h. Firing cycle in a laboratory furnace comprised a preheating step of 1 h at 100 °C, followed by a ramp to the maximum temperature at rate of 3 °C min$^{-1}$. The temperatures of 800, 900, 950, 1000, 1100 °C were maintained for 3 h. The cooling step was obtained by interrupting the cycle. One production brick from the factory has been also collected for SANS investigation.

### 2.2. Analytical methods

The simplest model of brick shaping by extrusion suggests that the plastic mass forced through a die presents an ellipsoidal front with maximum elongation aligned with the extrusion direction. In this way, typical ‘laminated’ texture develops (Bartusch and Händle, 2009). Thanks to their layer structure, phyllosilicates and clay minerals found in the raw clays are assembled into particles with a typical platelet-like morphology (Bergaya and Lagaly, 2006). For this reason, it is expected that they preferentially orient themselves with basal faces parallel to the extrusion direction (Bourret et al., 2015; Krakowiak et al., 2011; Maillard and Aubert, 2014), as schematically illustrated in Fig. 1.

The textural and microstructural features of the samples were observed in thin section under scanning electron microscope (SEM). The sections were cut oriented perpendicularly to the direction of extrusion (orientation B in Fig. 1). Investigations were performed with a FEI QUANTA FEG 450 instrument equipped with a backscatter electron, secondary electron and energy dispersive (EDS) detectors. The samples were coated with 5 nm thick gold film prior to analysis and observed at 20 kV accelerating voltage.

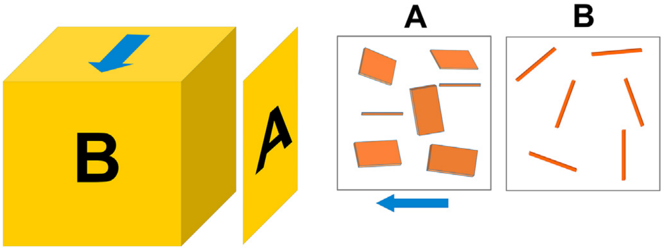

**Fig. 1.** Sketch of the sample orientation with respect to the extrusion direction (blue arrows) and expected orientation of the clay particles. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

SANS experiment was conducted at the KWS-2 instrument (Radulescu et al., 2015) operated by the Jülich Centre for Neutron Science (JCNS) at the Heinz Maier-Leibnitz Zentrum MLZ (Garching, Germany). Scattering curves were collected at 20 °C from 2 mm thick oriented slabs cut from the brick and the cubic samples. Samples were dried at 105 °C overnight and kept sealed in plastic bags until measurement. Slabs oriented perpendicularly to the direction of extrusion (orientation B in Fig. 1) were measured for all the firing temperatures and the production brick; in addition, slabs with orientation A, as illustrated in Fig. 1, were measured for the firing temperatures 950 °C and 1100 °C.

SANS data were recorded in the $Q$ range 0.0015–0.45 Å$^{-1}$, covered by merging data collected at wavelength $\lambda = 5.0$ Å with sample-to-detector distance 1.105 m and 7.605 m, and at wavelength $\lambda = 10.0$ Å with sample-to-detector distance 19.505 m. The scattering intensity ($I$) was collected on a 2-D detector as a function of the scattering angle, which defines the angular deviation of the scattered beam with respect to the incident direction. The 2-D raw data have been corrected for beam attenuation (according to measured sample thickness), the scattering from the empty cell, the electronic and background noise. Intensity was calibrated against a plexiglass standard material to set the data to absolute scale. Sample thickness was chosen in order to minimize multiple scattering effects (Hardman-Rhyne et al., 1984), therefore, no correction has been applied. Instrument data analysis and background subtraction was carried out using the QtiKWS software provided by JNCS.

#### 2.2.1. SANS data treatment and analysis

The SANS technique allows for the characterization of the microstructure of dense systems, such as fired bodies (Allen, 2005; Barbera et al., 2013; Barone et al., 2011; Botti et al., 2006; Renteria and Saruhan, 2006; Viani et al., 2016a). SANS arises because of the scattering contrast between the components in the investigated volume. What is probed is the fluctuation of neutron scattering length density (a measure of the interaction of neutrons with matter) within the sample. The technique represents an attractive alternative to using fluids to probe the pore space within samples, because a representative volume of sample can be accessed and the microstructure is probed in the entire volume investigated, including also potentially closed porosity. This volume is defined by the beam spot size (of the order of 5–10 mm) and the sample thickness. Details of the SANS theory can be found elsewhere (Glatter and May, 1999). Following a consolidated approach, for the characterization of the pore features in the samples it is assumed that the scattered intensity is proportional to the scattering contrast, adopting a two-phase approximation (i.e. matrix-pores), considering that the pores have much lower neutron scattering length density than the solid (Hardman-Rhyne et al., 1984). Chemical composition and skeletal density of samples have been used to calculate the scattering contrast as previously described (Viani et al., 2016b). Calculation using