**BRICKTECH: ASSESSMENT FOR THE USE OF WASTE IN THE BRICK PRODUCTION AND OPTIMIZATION OF THE FIRING CONDITIONS**

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**Cycle:** XXVIII

**Abstract**

BRICKTECH is a research project the main aim of which is improving the process of production of bricks, optimizing the firing conditions and enhancing the quality of the final product. The project is composed in 3 main parts: 1) analysis of mixtures created with pure phases and standard clays fired in the temperature interval between 550 and 1150°C for successive steps of 50°C to define a method to quantitatively describe microstructures and mineralogical composition and study the processes of nucleation and growth of mineral phases; 2) definition of an appropriate mix design for the production of bricks to be used in the restoration of the city wall of Castelfranco Veneto; 3) design of new industrial mixes produced: i) recycling and reusing wastes, ii) decreasing the firing temperature and consequently the CO₂ emission.

**Introduction**

Brick is a structural building material used in Italy since the Roman times. In the last years, extensive research has been conducted on the production of bricks with the main aims of promoting the environmental protection and supporting a sustainable development of this industrial sector. Many studies focused on the use of different types of industrial waste materials, and on the optimization of the firing temperature, as well as on the increase of the physical-mechanical resistance of the final products (Cultrone & Sebastián 2009, Demiz 2008, Eliche-Quesada et al. 2011, Eliche-Quesada et al. 2012, Fernandez-Pereira et al. 2011, Perez-Villarejo 2012, Raut et al. 2011, Topcu & Isikdag 2007, Zhang 2013). Nevertheless, the commercial production of bricks recycling waste materials is still very limited. In this frame, BRICKTECH represents a new research project which aims to develop a combined multianalytical approach for studying the relationships between mineralogical-textural and physical-mechanical characteristics and decay behavior (Calabria J.A. et al. 2009, Cultrone G. 2001, Cultrone G. et al. 2000, Duminuco P. et al. 1998, Maritan L. et al. 2006, Nodari L. et al. 2007, Riccardi M.P. et al. 2009), starting from the traditional and local brick productions (based on the regional availability of adapt raw clayey materials), to obtain new brick types to employ in the restoration of historical buildings and in modern constructions, and satisfying the necessity of the industry of saving energy, reducing the production costs, improving the quality of final products and preserving the shortage of raw materials reusing wastes and recycling according to the objectives of the Program of Research and Innovation - Horizon 2020.

**Analysis of mixtures obtain with pure phases and standard clays (Illite IMt-1 - Cambrianshale and Ripidolite CCA-2) at the Department of Geosciences of University of Padua, Italy**

**Materials and methods**

This study focuses on the microstructural and mineralogical analysis of 22 fired briquettes produced firing two different mixtures (M1 and M2), representing the average composition of the Veneto clays without and with organic matter (here carbon), at temperatures between 550 and 1150°C, with progressive steps of 50°C. More specifically, M1 and M2 were prepared according to the following compositions: M1 quartz 30 wt.%, calcite 25 wt.%, feldspar 5 wt.%, illite 24 wt.%; ripidolite 16 wt.%; and M2 quartz 28 wt.% , calcite 23 wt.%, feldspar 5 wt.% , illite 23 wt.% , ripidolite 15 wt.% , carbon 6 wt.%.

The fired briquettes were analysed in their micro-structure thought Scanning Electron Microscopy (SEM) and X-ray Powder Diffraction (XRPD) using the Rietveld method and 10 wt.% of zincite as internal standard, for a semi-quantitative mineralogical analysis.
Preliminary results and discussion

Mineralogy and texture

SEM back scattered electron (SEM-BSE) images of mineral and textural evolution of samples give an interesting picture of local phase transformation taking place at grain boundaries. No evident textural and mineralogical changes are observed in briquettes fired up to 700°C, after which calcite decomposes to produce, when large in size not to react with other phases, lime (CaO). In M2 the calcite decarbonation is delayed for the presence of the carbon, the combustion of which determined the emission of CO$_2$, which saturate the sample atmosphere and inhibits the decarbonation of calcite. Between 800°C and 900°C, quartz shows reaction rims composed of calcium silicate phases, whereas illite presents secondary bubble in his structure. Increasing the firing temperature, intergranular bridges occur between clay minerals and temper grains, where new mineral phases were observed.

Mineral phase analysis XRPD

The first variation of mineral assemblages in the fired briquettes appears between 500 and 650°C, with the progressive decomposition of ripidolite, while illite is completely destructurated at 950°C. The decomposition of calcite at 750–800°C, determined the crystallization of portlandite, for hydroxilation of lime, and for reaction with illite, chlorite and or quartz, of Mg- and Ca- silicates (wollastonite, Mg-Ca olivine and akermanite) in the 800–1100°C temperature range. Spinel is also produced in this temperature interval.

Semi-quantitative phase analysis (semi-QPA) bases on XRPD data was performed up to now on the mixture M1 and more precise quantification and analysis also of M2 products are in progress.

Subsequent steps

- Production of other mixes with the same raw material but different in grain-size to value the differences in the reactions evolution in the ceramic matrix;
- Qualitative and quantitative study of the relation between the different mixes in terms of boundaries reaction, kinetics of reaction, new phases growth, amorphous and porosity.

Characterization of mineralogical and chemical composition, physic proprieties and degree of decay of Italian commercial bricks, at the Department of Mineralogy and Petrology of University of Granada, Spain

Materials and methods

The study of a set of 5 industrial bricks (GP, N, R6, RSS and RS) produced in the Veneto region using local available clays adequately tempered, and obtained at different firing temperature, was addressed to the characterization of the product more used in the restoration of ancient buildings. GP and N are more carbonatic (45 wt.% carbonates v. 23 wt.% of quartz) and fired at higher temperature (1050°C), RSS and R6 (12 wt.% of carbonates v. 35 wt.% of quartz) and fired respectively at 950 and 600 °C, and, finally, RS is intermediate (20 wt. % of carbonates v. 35 wt.% of quartz) and it is fired at 980 °C.
Texture, mineralogy, chemistry, vitrification level and shape of pore were studied by Optical Petrographic Microscopy (UNI EN 11084), Field Emission Scanning Electron Microscopy (FESEM), X-ray Fluorescence (XRF) and X-ray Powder Diffraction (XRPD). The hydric parameters was performed using 15 cubic samples (50 mm per side) and 15 samples (25 x 25 x 120 mm). Water absorption and drying were determinate according to method described in UNI EN 772-7 (1998). Drying index (Di), apparent and real density, open porosity and degree of connection of pores were calculated. The distribution of pore access size (in the 0.001–100 µm range) was determined by Mercury Intrusion Porosimetry (MIP). Accelerated ageing tests were carried on 30 cubic samples (50 mm per side) to evaluated degree of decay: 30 cycles of 24 h duration were performed for freeze-thaw test (UNI EN 12371) and 10 cycles of 24 h duration for salt crystallization test (UNI EN 12370). Ultrasound propagation velocity was measured in order to evaluate the elastic-mechanical characteristics and structural anisotropy and check the modified degree of compactness during and after the ageing treatments.

Preliminary results and discussion

Mineralogical and chemical characterization

Macroscopically, samples RSS, RS and R6 are characterised by a red-coloured fine-grained paste, GP and N by a yellow and grey colour, respectively. Under the optical microscope, samples are texturally homogeneous, characterised by isotropic orientation, porosity abundance between 20-40%. Pores are generally small to medium in size with vesicles and vughs (rarely channels) shapes. The modal analysis of inclusions shows grain-size distribution moderately selected (for R6 and RSS) and not selected (for GP, N and RS). The volume of inclusions with respect to the groundmass is 40% for RSS, RS and R6 and 10-20% for GP and N. Concerning type of inclusions are of very similar for the sample fired at higher T (quartz, phyllosilicates, opaque minerals, feldspars, diopside, clay pellets), while R6 (fired at 600 °C) doesn’t show phases of high temperature (diopside). Chemical fluorescence analyses (% wt.) confirm the composition more carbonatic for samples N and GP, and more siliceous for the others. Mineral assemblages of the samples are determined on the basis of XRPD. RSS, RS, GP and N are characterized by similar phases that are quartz, gehlenite, anorthite, sanidine, diopside that confirm their high firing temperatures. R6 shows still present the peaks of muscovite, calcite and dolomite and there are no evident new silicate phases growth.

Hydric test and pore system

GP is the sample with the highest free and forced absorption values (A_f = 27.63%, A_r = 28.71%), N, RS and RSS show intermediate values, while R6 stands out for its low capability (A_f = 17.36%, A_r = 17.88%). RS shows a better interconnection (A_x = 2.12%) followed by N and RS. All samples dry within 200 hours and show very similar Di.

(1) Free water absorption, (2) forced absorption and (3) drying of the samples GP, N, RSS, RS and R6. Weight variation (ΔMM/M) v. time (in hours).

Hydric parameters of samples GP, N, RSS, RS and R6: A_f, free water absorption (%); A_r, forced water absorption (%); A_x, degree of pore interconnection (%); S, saturation coefficient (%); Di, drying index; p_o, open porosity (%); d_a, apparent density (kg m^-3); d_r, real (skeletal) density (kg m^-3).

Capillarity: trend of weight variation (ΔMM/M) v. time (in hours) at the beginning of the test. C, capillarity value, liquid mass absorbed per surface unit area (W, W_0)/A; K_c, coefficient of capillarity, m (g cm^-1) v. the square root of elapsed time (s) after 4 minutes of water absorption, B, capillary rise, h (cm) v. the square root of time (s) after 4 minutes of water absorption.
The MIP, combined with the information obtained at the microscope and by the hydric tests, allowed to completely describe the pore system of the bricks. Values of open porosity ($p_o$), apparent and skeleton density ($d_a$, $d_sk$) are similar to those measured by hydric tests. Modal analysis divides samples in 3 groups all with maximum radius close to 1 µm: 1) GP and N are unimodal; 2) RS and RSS show a bimodal trend; 3) R6 is characterized by porosity less selected from 0,001 to 1 µm.

Values of MIP on samples GP, N, RS, RSS and R6: $p_o$, open porosity (%); $d_a$, apparent density (kg m$^{-3}$); $d_sk$, real (skeletal) density (kg m$^{-3}$).

**Compactness and durability**

Ultrasonic velocity tests show the dynamic behaviour of samples. The propagation velocities $V_p$ (compressional pulse) and $V_s$ (shear pulse) were measured to obtain information on the degree of compactness of the bricks and on their durability.

Once established wave velocities ($V_p$ and $V_s$) and density, Structural Anisotropy ($\Delta M$), Poisson Coefficient ($\nu$), Young (E), shear (S) and bulk (K) modules were calculated on dried samples. $V_p$ pulses were measured in regular step during the cycles of ageing tests to evaluate the damaging effects with weight changes.

First set of data about freeze-thaw test (in total 30 cycles) indicates that brick R6 is the less durable, with higher weight loss and development of internal cracks (no transmission of pulses in sound tests).

**Subsequent steps**

- Field Emission Scanning Electron Microscopy (FESEM) for characterising the microstructures and the degree of vitrification of the bricks;
- Accelerated aging tests (freeze-thaw and salt crystallization cycles);
- Monitoring and assessment of durability (sound tests, colorimetry, MIP)
Future plans

The research will carry on with the following projects:

i) Cases of study: “Castelfranco Veneto bastions” (TV). Mineralogical and physical characterization of original damaged bricks and development of suitable “mix design” for replacement in restoration.

More in detail the work will be divided into:

- Historical documentation
- Assessment of decay in situ (Visual inspection, Thermography IR, Sound tests)
- Mineralogical and chemical analysis (Optical Microscopy, Scanning Electron Microscopy, X-ray Fluorescence, X-ray Powder Diffraction, µ-Raman)
- Physical-mechanical features (compressive and flexural strength, “creep” resistance, hydric behaviour, aging accelerated tests, Mercury Intrusion Porosimetry, Computed µ-Tomography)
- Firing test with local raw material to obtain a new mix design for replace damaged bricks with new products with apposite physic and aesthetic features

ii) Assessment of reuse of waste material in brick production and optimization of firing conditions:

Firing test at different temperature on new experimental “mix designs” obtain through: i) reuse of trachyte wastes of quarry, ii) use of organic wastes as agents-porosity forming. More in detail:

- Qualitative and quantitative analysis of mineral and amorphous phases growth during firing (Optical Microscopy, Scanning Electron Microscopy, X-ray Fluorescence, X-ray Powder Diffraction, µ-Raman);
- Study of evolution, shape, distribution and 3D morphology of porosity (Digital Imagine Analysis, Mercury Intrusion Porosimetry, Computed µ-Tomography)
- Mechanical features (compressive, strength and “creep” resistance)
- Physical features and prediction of decay (anisotropy, sound test, thermal conductivity, linear shrinkage, hydric behaviour, accelerated aging test, salt crystallization and freeze-thaw tests)

Part of this research will be carried out at the Departamento de Mineralogìa y Petrologìa de l’Universitad de Granada”, Spain, in collaboration with prof. Giuseppe Cultrone.

References


CULTRONE G., SEBASTIAN E. 2009, Fly ash addition in clayey materials to improve the quality of solid bricks, Construction and Building Materials 23, 1178-1184


SUMMARY OF ACTIVITY IN THIS YEAR

Courses:
SALMASO L., CORAIN L.: “Corso di statistica applicata alle scienze”, Università degli studi di Padova
CALANDRUCCIO E.: “Corso di inglese parlato”, Università degli Studi di Padova
GULIK L.: “Corso di inglese scientifico”, Università degli studi di Padova
DALCONI C.: “Analisi quantitative con metodo Rietveld”, Università degli Studi di Padova

Schools and conferences:
EMU SCHOOL “MINERALS AT THE NANOSCALE”, 3 - 6 June 2013, Granada, Spain
1st JOINT SIMP-AIC INTERNATIONAL SCHOOL, 4 - 8 September 2013, Camerino, Italy
12th EUROPEAN MEETING ON ANCIENT CERAMICS (EMAC 2013), 18-21 September 2013, Padova, Italy

Posters:

Grants:
- SIMP Grant for EMU SCHOOL “MINERALS AT THE NANOSCALE”, 3 - 6 June 2013, Granada, Spain.
- Grant of mobility “ERASMUS PLACEMENT”; 23 September - 23 December 2013, at the “Departamento de Mineralogia y Petrologia de l’Universidad de Granada”, Spain.