BRICKTECH: ASSESSMENT FOR THE USE OF WASTE IN THE BRICK PRODUCTION. PETROPHYSICAL CHARACTERIZATION OF NEW MIX DESIGNS AND OPTIMIZATION OF THE FIRING CONDITIONS

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INTRODUCTION

Brick, a ceramic product used as a building material since ancient times, is still valued for the easy availability of geo-resources, for the resistance to loading and environmental stress, and for its aesthetic qualities. During firing, the raw materials, a mixture of a body of clay minerals and predetermined fractions of silt and sand (temper), is transformed into a new artificial material in which mineralogical changes occur, similar to those developing during pyrometamorphism; as regards microstructure, new porosity develops and melt forms (Riccardi et al., 1999; Aras, 2004; Cultrone et al., 2004; López-Arce & García-Guinea, 2005).

Although several studies on ceramic materials have been carried out (Duminuco et al., 1998; Riccardi et al., 1999; Elert et al., 2003; López-Arce et al., 2003; Cardano et al., 2004; Aras, 2004; Cultrone et al., 2004; Cultrone et al., 2005a; Cultrone et al., 2005b; Maritan et al., 2005, 2006; Miriello & Crisci, 2007; Setti et al., 2012; Cultrone et al., 2014), and many other have been conducted on the industrial brick production focusing on environmental protection and supporting sustainable development (Dondi et al., 1997a, 1997b; Demir, 2008; Cultrone & Sebastián, 2009; Raut et al., 2011; Eliche-Quesada et al., 2012; Zhang, 2013; Muñoz Velasco et al., 2014a, 2014b; Neves Monteiro & Fontes Vieira, 2014; Bories et al., 2014), little research has been addressed to the real needs of brick industries.

This work aimed to close this gap, in collaboration with the personnel of an Italian brick factory (SanMarcoTerreal srl), focusing on actual requirements in industrial research, i.e., the creation of new mixes for specific situations (e.g., restoration of historical buildings), and on the optimization of green-solutions in order to promote a sustainable development in terms of saving resources and energy.

The principles of a sustainable development arise from the increasing shortage of non-renewable resources exposing well-being of the future generations to risk, and encompass the concepts of “Reuse, Recycle and Replace” improving environmental damage control (Ortiz et al., 2009; Haldar, 2013). The sustainability of a product is evaluated considering the interactions with the environment, taking place during the entire cycle of its life (Life Cycle Assessment, LCA), from raw material extraction to disposal, recycling or reuse. It includes energy and material consumption, environmental risk factors, specifically related to gas emissions during firing and to the release of chemicals, exposing humans and environment to risk (Koroneos & Dompros, 2007; Peris Mora, 2007; Ortiz et al., 2009).

The great amount of wastes generated by industrial processes and the increasing attention to environmental issues stimulated a progressive interest in the reuse of wastes. Moreover, the increasing demand of sustainable materials addressed research to develop environmental friendly construction materials, using wastes and at the same time introducing better quality bricks in the industrial production.

The absence of standard procedures fulfilling requirements of industrial production and widespread general public scepticism are the main weaknesses for scaling-up. Despite these difficulties, scientific research should continue investigating the possible reuse of wastes, maintaining required quality and health standards of the final products, finding valid criteria of standardization of the technical properties, and quantifying the impact on economic and environmental issues, thus allowing aware eco-labelling and adequate public education (Burnett, 2007; Zhang, 2013).
This work relied on an accurately designed multi-analytical approach and investigated the properties of five bricks, already on the market, furnished by the SanMarco Terreal factory, in order to have a solid basis to tackle the actual industrial challenge for identifying methods and criteria to introduce green solutions and to ensure a leader industry, promoting excellence and innovation. Moreover, part of the research focused on the study of the pore structure since it represents one of the principal features affecting the building material quality, and therefore needs to be evaluated when predicting bricks durability. With this in mind, new mix designs were produced reusing wastes. The choice fell on two kinds of waste, which both do not generate undesirable pollutant emissions or release contaminants, therefore ideal in terms of environmental and human acceptance:

(i) trachyte fragments from quarrying activity (Euganean Hills, Rovolon, Padova);
(ii) ceramic sludge resulting from the ceramic industry.

This research was motivated from real interest of the brick factory of finding alternative and eco-friendly additives to be used instead of the standard quartz sand to produce eco-bricks, in substitution of those traditionally produced, characterized by appropriated mechanical and aesthetical properties and durability.

METHODS

In all samples, texture, mineralogy and degree of vitrification were characterized by polarized light microscopy (POM), scanning electron microscopy (SEM) equipped with EDS microanalysis system, X-ray fluorescence (XRF) and X-ray diffraction (XRD).

The following physical-mechanical properties were also studied: i) the colour variation between dried and wet fired bricks was measured using a Konica Minolta CM-700d spectrophotometer following the CIELab system according to the UNE EN 15886 (2011); ii) the water behaviour (free and forced absorption) was determined according to UNI EN 13755 (2008); iii) the drying index was measured following the NORMAL 29/88; iv) the capillarity was determined according to the UNI EN 1925 (2000); v) the strength resistance and the anisotropy degree were measured adopting destructive and non-destructive techniques (uniaxial compression following the UNI EN 1926, 2007, and ultrasound propagation).

Infrared thermography (IRT) was also performed in order to evaluate brick thermal insulation using a FLIR T440 series camera.

Porosity of the bricks was determined by combining the results of hydric tests with those obtained from mercury intrusion porosimetry (MIP), nitrogen adsorption (AN), image analysis (DIA) studying images obtained by scanning electron microscopy (SEM) and 3D models developed by computed microtomography (micro-CT).

In addition, all samples were subjected to accelerated aging tests: freeze-thaw cycles (UNI EN 12371, 2010) and salt crystallization (UNI EN 12370, 2001) were carried out in order to measure the resistance to deterioration.

SUMMARY OF RESULTS

Due to the different aspects of the brick production analysed, results of the thesis are here presented in four different sections.

How to face the new industrial challenge of compatible, sustainable brick production: study of various types of commercially available bricks

A set of 5 industrial bricks, currently on the market, obtained by different raw clay materials, and fired at different temperatures were studied: i) two carbonate-rich bricks, fired at higher temperature (1050 °C); in one of them 10 wt.% of MnO₂ was also added; ii) two carbonate-poor bricks fired at 950 and 600 °C, respectively; one brick with intermediate carbonate content fired at 980 °C.

The mineralogical composition of the bricks resulted to be related more to the firing temperature than to the initial composition of the greens (clay + temper).
More in detail, all the samples fired over 900 °C are characterized by a occurrence of quartz, wollastonite, gehlenite, plagioclase, K-feldspar, and diopside, even if in different proportions among the samples.

Brick fired at 600 °C still contains phyllosilicates (chlorite and illite), calcite and dolomite. As for the feldspars, systematic differences were observed between bricks fired at low temperature (600 °C), in which orthoclase from the raw material persists, and those produced at higher temperature (900-1050 °C), in which sanidine, a more stable high-temperature polymorph, formed; moreover plagioclase was characterized by a more anorthitic composition.

Microstructurally, samples fired above 900 °C showed partially melted groundmass and bridging, as well as reaction rims (corona-like structure) formed by new mineral phases, such as gehlenite and diopside, around carbonate inclusions in contact with quartz, feldspar, and phyllosilicates. Physical-mechanical properties resulted to be closely dependent from the firing temperature, the nature and quantity of mineral phases, a well as the microstructure. In detail, the sample fired at 600 °C stood out for its low absorption and capillarity rise, and highest anisotropy caused by the presence of phyllosilicates. With the increasing firing temperatures, samples became texturally more homogeneous and anisotropy decreased, as attested by the increasing ultrasonic waves’ velocities. Samples fired at temperatures above 950 °C had the best mechanical features (Young, Shear, and Bulk moduli), which resulted to be closely related to the formation of new silicates and the increase of amorphous phases. Data from freeze-thaw and salt crystallization tests indicate that sample fired at 600 °C was the weakest, for the loss of fragments and development of fissures and cracks, whereas those fired at higher temperature were more durable.

*Combined multi-analytical approach for the study of the pore system of bricks: how much porosity is there?*

Four industrial bricks were studied in order to determine the distribution and the geometry of the pore system. These bricks were obtained from two types of clays, which differ in terms of carbonate amount: two bricks were produced from a moderately carbonate clay with the same mineralogical composition of the “green”, but with two different firing temperatures (600 °C and 950 °C, respectively); two bricks were produced from a highly carbonate clay, both fired at 1050 °C, but with different composition, due to the addition, in one of them, of Mn-oxides as grey-dye.

The characterization of the pore structure is difficult because pores have different shapes, sizes, interconnection, and the material surface, and also because each analytical technique allows to determine restricted aspects of the pore system due to different instrumental limitations. For this purpose the study was carried out using different methods, either “direct” or “indirect”, to develop a general characterization of the porous system and overcome their differences and limitations (mainly pore sizes and shapes). Mercury intrusion porosimetry, nitrogen adsorption and hydric tests are considered “indirect” methods, because based on the behavior of fluids inside the material and, therefore, evaluate only interconnected pores (open porosity). Digital image analysis (obtained by SEM-BSE images at magnification of 50x and 500x) and micro-computed tomography are considered “direct” techniques and allow to observe the shape of the pores and to measure the abundance of both open and closed porosity.

Through this multi-analytical approach it was possible to describe the pore system of each samples and demonstrate in detail the close relationship between pore evolution and the raw composition of bricks and firing temperatures reached in the production process. Moreover, “overlapping zones” were identified according to the image resolution established for the digital imaging and the micro-CT analysis, which allowed to compare the various methods and to define their differences.

Results showed that bricks made with the highly carbonate clay had the highest amount of open porosity due to the carbonate decomposition during firing, which promotes the formation of porosity and of pore interconnection. Moreover, due to the high firing temperature (1050 °C) big and rounded-shaped pores formed, in relation to the release of gas and to the presence of amorphous phase which conferred viscosity to the system allowing the pores to expand and not to be confined between mineral boundaries or discontinuities. On the contrary the brick made with the moderately carbonate clay and fired at 600 °C, presents less homogeneous
shaped and smaller pores because at this firing temperature most of the typical reactions of clay mineral decomposition and formation of new silicates and melt had not occurred, yet. Finally, the brick with the same composition but fired at 950 °C showed an intermediate situation and was characterized by a higher complexity of pores, with presence of both small and large pores.

**Recycling trachyte waste from quarry to brick industry: petrophysical characterization and durability of new ceramic products**

Bricks obtained using a carbonatic clay added with trachyte sand (size range comprised between 0.16 and 0.4 mm), with three different proportions 5%, 10% and 15 wt.%, were fired at three different temperatures, normally adopted in the production implant (900, 1000, and 1100 °C) to determine the relationship between the percentage of the added temper, the firing temperature and the physical-mechanical properties of each produced brick.

Under the mineralogical point of view the all samples were composed by quartz, sanidine, diopside, wollastonite and gehlenite, as well as amorphous phase, in various proportion. Hydric absorption behaviour decreased for samples with the highest content of trachyte (15 wt.%) and an overall poor interconnection of pores was found.

Open porosity, determined by the hydric tests, decreased with increasing either firing temperature and the trachyte content; this behaviour was interpreted as related to the higher content in amorphous phase. Trachyte acted as a fluxing agent and determined the partial melting of the matrix (originally clay minerals) for diffusion of alkali from the feldspars phenocrysts and trachyte groundmass. The nitrogen adsorption isotherms detected a texture characterized by micro- and meso-pores that became larger and more round with increasing firing temperatures and trachyte contents. This was also detected by the evolution of the texture and the pore system observed by SEM, where it was also observed how the high content of trachyte promotes melting due to the presence of alkali feldspars. All bricks had good physical and mechanical properties according to the uniaxial compression test and ultrasound velocities, and high structural anisotropy. In addition, accelerated ageing tests (freeze-thaw and crystallization of salts) showed high resistance to stress conditions, without presenting damage to the last test cycles. Infrared thermography, here used to analyse the thermal effusivity, suggested a tendency of materials to reduce susceptibility to heat in samples with increasing trachyte content, except for the sample in which the combination of the high trachyte content (15 wt.%) and high firing temperature (1100 °C) induced a higher sintering of the matrix and a reduction in quantity of pores, both promoting heat conductivity.

The aesthetic aspect of these bricks, as measured by colorimetry, demonstrated that all the bricks could be used without problems also in comparison with the ordinary bricks, which are nowadays produced industrially.

**Use of industrial sludge in brick production: effects on aesthetic qualities and physical properties**

A brick produced with the addition of sludge was compared with two industrial bricks fired at the same temperature (1050 °C) and obtained from the same illitic-chloritic carbonatic clay: i) a yellow coloured one, obtained by mixing the clay with high content of carbonates and 10 wt.% of a siliceous sand (temper); ii) a dark brick obtained using the same mixture of the former, but adding also ~ 15 wt.% of hausmannite (Mn2O3) as dye.

The two industrial bricks were both composed of predominant quartz, abundant gehlenite, diopside and wollastonite, and associated anorthite, sanidine, hematite, and amorphous phase; the brick obtained with the addition of Mn3O4 contained also bustamite (CaMnSi2O6), a Mn-rich high-temperature polymorph belonging to the wollastonite group, developed from the reaction between hausmannite, carbonate and quartz. The new designed brick with sludge had the same mineral composition, with the exception of bustamite, but the newly formed silicates and the amorphous phase were less developed.

Colorimetry tests showed that the brick with sludge had a similar aesthetic appearance with the yellow commercial brick. Although colour changed in all cases, the new brick, compared with the others, had the advantage of changing its aesthetic aspect to a lesser extent in wet conditions (i.e., rainfall or humidity).
Concerning the water behaviour, the brick with sludge had the best pore interconnection and a slightly higher open porosity, confirmed by mercury intrusion analysis. Analysis of smaller sized pores by nitrogen adsorption indicated that it was characterized by the highest open porosity, and contained less micro-pores. On the contrary, the brick with the lowest open porosity, showed adsorption-desorption isotherms with the highest values, indicating that the greatest number of micro-pores was present in that containing bustamite. This evidence indicated that the addition of sludge determined lower micro-porosity than the other two bricks; instead, the addition of manganese oxide is responsible for the increase of micro-porosity.

Uniaxial compression test demonstrated that brick with sludge had a value of stress ($\sigma$) of 15.20 N mm$^{-2}$, almost equal to that of the yellow brick (41.80 N mm$^{-2}$), whereas the dark brick had a higher value (18.73 N mm$^{-2}$) probably due to the content of manganese oxide, which increased the mechanical strength. These good mechanical properties were also confirmed through ultrasounds.

During the salt crystallization test the brick with sludge maintained almost intact its appearance and increased in weight, suggesting that a larger amount of salts accumulated during the test, probably because of the different size range of pore. On the contrary, under freeze-thaw conditions a progressive decay was verified up to the 20th cycle, until the total disintegration of the samples at the end of the test (30 cycles).

CONCLUSIONS

The multi-analytical approach, adopted to study both the industrial and the new designed bricks, highlighted close relationships among mineralogy, porosity, as well as physical properties and their behaviour in different stress environments. In the commercial brick fired at the low temperature (600 °C), the absence of new silicates and the poor bonding among grains due, to the lack of melting during firing, determined the brick to be the weakest in load resistance and decay tests. Conversely, bricks fired at temperatures above 1050 °C showed the greatest mineralogical changes, with crystallisation of new silicate phases and widespread vitrification of the matrix. This improved physical-mechanical properties of the bricks, but determined rather high water absorption and capillarity rise. The use of hausmannite ($\text{Mn}_3\text{O}_4$) as a dye caused changes not only in the visual aspect of the bricks, which turned dark grey in colour, but also in the mechanical properties and structure of the pore system, since haummanite promoted vitrification during firing.

The combined analytical approach of direct and indirect methods for the study of the porosity permitted to have a more complete view of the pore system in terms of both size and morphology. It was verified that pore system (both in pore size and shape) was different according to raw materials used and firing temperature adopted. This part of the research represents a starting point to define a protocol for the quantification of voids, being an important contribution for brick industry interested in the optimization of porosity (e.g., in relation of different environment conditions and durability). Moreover, this detailed comparison between different methods allowed to better point out the limits and advantages of each technique. Bricks made with carbonate-rich clays have the higher open porosity and pore interconnection determined by the carbonate decomposition. The increase of the firing temperatures also favoured volatile release and caused significant changes in pore morphology by developing large rounded pores. On the contrary, clays with lower amounts of carbonate produced materials characterized by a less homogeneous porosity and also by smaller pores.

The use of trachyte as temper, especially at high percentage (15 wt.%), favours vitrification at lower firing temperature for the fluxing effect of alkali feldspars. This idea was supported by textural observations, revealing an increased number of bridges connecting adjacent grains, the development of a more compact matrix in correspondence of trachyte grains, the increase of the apparent density, and the evolution of the texture. The pore system of such new bricks, as observed by SEM, showed that increasing firing temperature and trachyte content, pores become larger and rounder. The correlation between brick resistance and both firing temperature and trachyte content arose also from the uniaxial compressive strength that was linked to the increase in compactness due to vitrification related to the presence of feldspars contained in trachyte temper. All bricks displayed high resistance to decay under aggressive environmental conditions (freeze-thaw and salt
crystallization) without damage. The good response to stresses and the lack of significant differences among the samples proved that trachyte could be considered as a reliable alternative material to replace expensive fluxing agent materials. The use of trachyte allowed preparing bricks with appreciable properties, already after firing at 900 °C, and containing more than 10 wt.% of trachyte, therefore saving in terms of energy, costs, and environmental resources.

Also in the case of reuse of ceramic sludge, the possibility of adding waste material in brick mixture gave satisfying results. Colorimetry tests showed that bricks with sludge have similar aesthetic appearances as some yellow bricks manufactured by the company, suggesting that its colour closely resembles traditional bricks. Uniaxial compression and ultrasonic tests showed that the mechanical resistance was very similar to that of commercial yellow bricks, indicating that despite the change of temper also mechanical properties were preserved. The most problematic aspect arose from the durability tests. Although during salt crystallization test bricks with sludge maintained their appearance without evident damages, after a number of freeze-thaw cycles bricks faced progressive decay until total disintegration at the end of the test. This suggested that this type of bricks might be considered as a valid substitute of commercial ones for their mechanical properties, aesthetic qualities and water behaviour, but may suffer in cold climates.

Beyond the successful results obtained and the feasibility of new bricks, this work is an example of how university and the industrial realities can collaborate pursuing common objectives. The interest in addressing research and scientific growth to support sustainability and environmental compatibility derived from the shared certainty that margins exist to improve construction materials through the introduction on the market of eco-conscious productions. This study specifically demonstrated the possibility of recycling waste in the production of bricks, maintaining traditional aesthetical characteristics and economising in terms of both exploitation of new resources and production costs, as well as ensuring sustainable processes and materials.

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