Ancient bricks technologies: improving the built heritage conservation at high humidity areas

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Yellowish hue bricks used at the Basilica of Saint Justina of Padua (Northern Italy) produced during the 5-6th centuries (Late Antiquity times) were analysed: i) bricks located at the original placements, very humid areas where the environmental conditions remain almost constant during the day, and ii) reused bricks placed at Medieval walls exposed to insolation and quite fluctuating conditions. The first displayed good conservation state and a pale yellowish colour. The reused bricks shown granular disaggregation and a dark yellowish colour. The formation of zeolites as hydration products were detected in the pale and dark pastes. The better preservation of these bricks under humid environments, related to zeolites formation, is suggested. The data achieved could be transferred to current ceramic industry in order to produce high-quality bricks particularly appropriate for the built heritage conservation located at high humidity areas.

Key words: high-quality bricks, secondary phases, zeolites, cementious properties, high humidity areas

I. INTRODUCTION

Ceramic technology implies mineralogical and microstructural changes that entail more complexity during the firing of Ca-rich clays than of Ca-poor clays [1]. The properties of ceramics can be improved by mixing base clays or adding temper, such siliceous and carbonates inclusions or crushed ceramic [2].

Calcareous clays result in ceramics with exceptional porosity, mechanical behaviour and weather resistant [3]. New-formed minerals and amorphous phase are the products of the solid-state reactions that occur at high firing temperatures between phyllosilicates and carbonates [1]. Besides the mineral phases preserved from the base clay and those formed during firing, ancient ceramics could contain secondary phases crystallised after firing, both associated to the high temperature phases transformation and precipitated in porosity from aqueous solutions.

The post-depositional transformations are mainly related to both the chemical-physical conditions of the environment, and in particular of the groundwaters composition [4], and the mineralogical and textural features of ceramic material. The crystallisation of secondary mineral phases, at the surface and/or through open porosity, may change the colour, mineralogical composition and microstructure of the ceramic bodies [5]. The reuse of bricks often induces the change of the environmental conditions in which the bricks were initially settled, with consequent decay.

II. MATERIALS AND METHODS

A. Padua's placement

Since the Late Bronze Age, the territory of Padua has been occupied by human settlements. Its geographical centrality in the Veneto region (Northern Italy) and the abundant fluvial channels that run through the area, have fostered its development. The city of *Patavium* was a strategic trade area during the Roman times. Between the 5th and 10th centuries, periods of depopulation and reactivation were occurred in the city. During the 13th century, framed on the Communal period, a deep urban awareness was developed [6]. The University was then founded (1222) and numerous churches, towers, public buildings and private residences were built, as the Palazzo della Ragione (1218-1306), the medieval wall (1195-1210) or the Basilica of San Antonio (1232-1310). Within such intense constructive activity, the reuse of Roman bricks was a very extensive practise.

Padua is located in the Eastern side of the *Pianura Padana*, covered mainly by Quaternary deposits. The abundance of clay materials has conditioned most of its constructions choices (use of brick), as well as the ceramic industry leadership of Northern Italy. Padua has a warm and tempered climate. The rainfall is significant throughout the year, with an average annual of 867 mm. The average temperature is 13 °C and the average annual relative humidity is 73 %.

B.   The Basilica of Saint Justine of Padua

The Abbey of Saint Justina stands next to the Prato della Valle square (Fig. 1a). By the 6th century, a small basilica was built where Saint Justina of Padua had been buried, and a chapel (sacello) was attached. The sacello, its apse and a mausoleum were preserved [7].
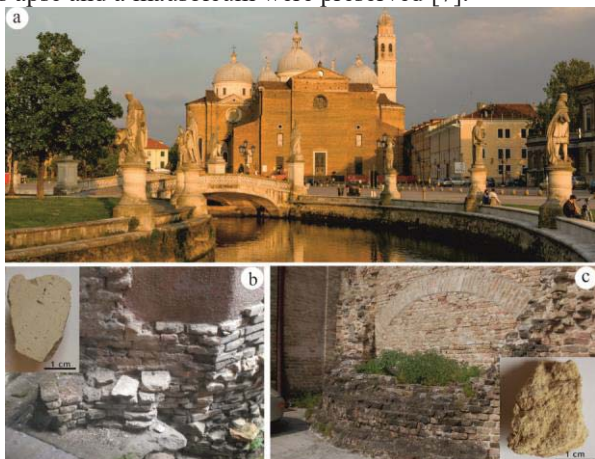

Fig. 1. Location of the studied bricks. a) Basilica of Saint Justine of Padua, next to Prato della Valle, b) apse of the Late Antiquity sacello (detail of the pale yellowish bricks), c) Eastern wall of Saint Sigismund Medieval chapel (detail of the dark yellowish bricks).

By the 10th century, there was already a Benedictine monastic community next to the basilica and in the 12th century the basilica underwent an important reconstruction, after major damage caused by the earthquake of 1117. During the 12-13th centuries, the Romanesque construction focused on the presbytery, the bell tower and Saint Sigismund chapel. The current basilica was built during the 16th century. Nowadays, the Benedictine community cares and preserves the complex.

C.   Yellowish hue bricks sampling

Five bricks from the areas dated to the Late Antiquity (inner mausoleum and external apse of the sacello) and five from the Medieval Eastern wall of Saint Sigismund chapel were studied (Figs. 1b and 1c). High humid conditions were measured at the Late Antiquity areas (65% RH and 27°C, 9 June 2019 at 11:30 am). Furthermore, they are quite closed areas where the environmental conditions remain fairly constant throughout the day. The outer Eastern wall of Saint Sigismund Medieval chapel is exposed both to an important insolation degree and to a major fluctuation of the environmental conditions of the city. On 9 June 2019 at 9:30 am, 48 % RH and 28°C were measured. Besides, this wall is just faced to an internal parking area. Macroscopically, bricks from the Late Antiquity areas show a good conservation state and a pale yellowish hue, whereas those from the Medieval wall display granular disaggregation and colour darkening.

D.   Analytical techniques

Ceramic pastes were analysed by X-Ray Powder Diffraction (XRPD) and Scanning Electron Microscopy - Backscattered Electrons mode (BSE) -with Microanalysis in Energy Dispersive X-Ray Spectroscopy (SEM-EDS). The mineralogical composition was determined using the PANalytical X'Pert PRO diffractometer, equipped with a Co X-ray tube and a X'Celerator detector, in the 3°-70° 2θ range, step size 0.02° and 1s counts per step. Mineral phases were identified using the X'Pert HighScore Plus software. The microstructure and the chemical elemental composition were studied by means of an SEM CamScan MX 2500 microscope coupled with a Genesis Energy Dispersive X-ray Spectrometer.

III.   RESULTS AND DISCUSSION

A.   XRPD analysis

The mineral phases determined by XRPD are shown in Fig. 2. Quartz and K-feldspar were residual compounds of the raw clay; high temperature phases consisted of anorthite, diopside, gehlenite, mullite and hematite; whereas calcite, zeolites (analcime and chabazite) and gypsum are secondary phases. The pale and dark yellowish bodies displayed very similar mineralogical assemblage. Anorthite, diopside, analcime and calcite were the predominant phases; gehlenite and mullite were important. Chabazite was also detected in the pale pastes. Quartz and K-feldspar concentrations were higher in the dark bodies, while their content was significantly lower in the pale bodies. In the dark pastes, the presence of gypsum as well as the reduction of gehlenite, calcite and mullite contents were noted for some samples.

The significative presence of the aluminocalcosilicates and calcium/magnesium silicates detected pointed out that mixes of Mg-rich calcareous clays and illitic-kaolinit raw clays were used and that firing temperatures of 950-1000 °C were reached. In the pale yellowish hue pastes, quartz was almost consumed on reactions yielding to high temperature phases formation, suggesting that the illitic-kaolinitic clays were also Si-rich. The importance of such new-formed phases may suggest the presence of carbonate inclusions, being the local sands rich in carbonate rocks.

As dolomite partial decomposition into periclase occurs around 750-800 °C and the decarbonation of calcite into lime is completed up to 900 °C, the calcite mineral phase detected in the analysed bodies may largely correspond to secondary calcite. This, therefore represents the calcium carbonate recarbonated after relicts of lime, from the surrounding aqueous solutions that flow where the bricks were placed and/or from the joint mortars.

Also, Ca-rich microsites enhanced by gehlenite and its solubility in the presence of acetic or humic acids, may foster secondary calcite formation [5,8,9].

It should be considered that for calcite-rich systems, when the pastes contain coarse calcite grains and/or if the heating rate is rapid, calcite decarbonation may extend to 1000-1100°C [10]. Therefore, the contemporaneous occurrence of primary calcite and neo-formed phases is justified by such kinetic and thermodynamic considerations.
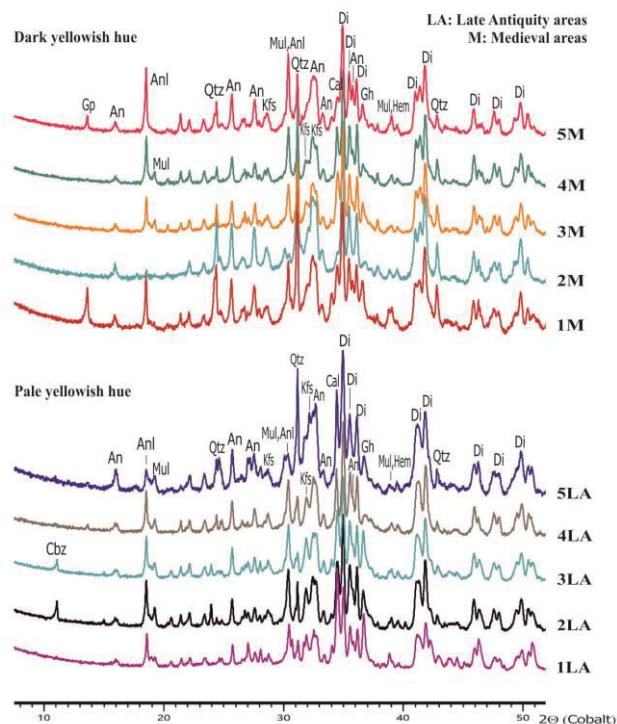

Fig. 2. XRPD patterns of the pale and dark yellowish hue pastes. Quartz (Qtz), K-feldspar (Kfs), anorthite (An), diopside (Di), gehlenite (Gh), mullite (Mul), hematite (Hem), calcite (Cal), analcime (Anl), chabazite (Cbz) and gypsum (Gp).

Buxeda et al. [11] describe Na-zeolite (analcime) formation in highly fired sherds (>1000 °C) subjected to burial environments as a selective alteration and contamination process where the potassium leaching and the sodium fixation are involved. In the analysed pastes, the noteworthy presence of aluminium and calcium suggest rather the formation of zeolites such wairakite ($CaAl_2Si_4O_{12} \cdot 2H_2O$), whose XRPD pattern is similar to that of analcime, and Ca-chabazite (($Ca_{0.5}$,Na,K)$_4$[$Al_4Si_8O_{24}$]$\cdot 12H_2O$). Moreover, with the passing of time, gehlenite is decomposed and could be transformed into wairakite as well [9].

The gypsum occurring in some dark yellowish pastes may be related with bricks placement, in front of the parking area. As they are very exposed to vehicles exhausts, airborne SO_2 emitted by diesel engines may led sulfation processes on bricks [12].

B. Microstructural analysis

The pale yellowish bodies shown a fine grain microstructure with a low vitrification degree (Fig. 3a). Sub-rounded pores were observed, some surrounded by rims that seem to be material previously molten [13], some partially filled that mainly correspond to secondary porosity resulted from decarbonization and densification of the pastes [14]. The particles were dispersed in a highly dense micromass mainly constituted by Ca-plagioclase crystals (Fig. 3b). Quartz and k-feldspar residual grains show dissolution and phase transformations at grain boundaries. Inclusions formed by calcium-magnesium silicates with iron contents and Mg-rich particles highly porous - both with reaction rims - were observed (Figs. 3c and 3d).
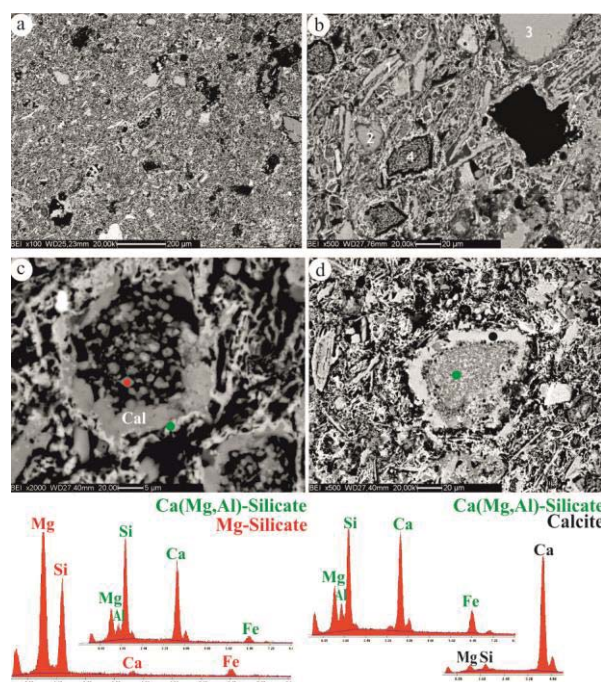

Fig. 3. SEM-BSE images and EDS analysis of the pale yellowish pastes. The fine grain micromass is chiefly composed by Ca-plagioclase crystals (1), quartz (2) and k-feldspar (3) residual grains and carbonatic inclusions, most of them very rich in Mg (4).

These particles correspond to the original carbonatic inclusions (with calcitic and/or dolomitic composition), that were differently transformed during firing trough dolomite decomposition into calcite and periclase as well as lime released from calcite decarbonation. As diffusion rate of lime is higher than periclase, is consumed faster, so Ca-Mg silicates begin to nucleate inside the carbonatic grains. As temperature further increases, more lime is released, so more calcium–magnesium silicates are formed, shaping bright rims as they also uptake iron from the melt. Such process leads an important degree of porosity inside and around the dolomitic particles.

From the excess of periclase that remained inside the particles, two possibilities are suggested for Mg-silicates nucleation: i) at expense of the calcium–magnesium silicates already formed, that reacted with periclase and were transformed into magnesium silicates [1], such Mg-olivine phase (forsterite), ii) by periclase reaction with silica, forsterite was formed.

As lime recarbonates faster than periclase [15], secondary calcite formation from lime recarbonation during firing is suggested. This calcite filled totally the porosity around some pristine carbonates and calcite light rims were developed (Fig. 3d).

In any case, secondary calcite was also precipitated in the porosity rims formed around pristine carbonatic inclusions, mainly related to aqueous solutions flowing where the bricks were placed. As periclase formation occurs between 700 and 1000 °C and could be also formed due to decomposition of other Mg-rich minerals like diopside, akermanite and/or forsterite [16], MgO may be supplied during almost the firing process. Therefore, the magnesium seems to be the element most widely involved in the formation of the new phases, as it was already stated elsewhere [17].

As silica, alumina, lime and periclase were incorporated into the newly-formed phases, the melting process was blocked at high temperature, so an early stage of vitrification was achieved [18]. Even though carbonates obstruct the vitrification at high temperatures, they enhance the development of a stable microtexture up to 1050 °C [19].

The presence of rounded calcite inclusions circa 1 mm in size should be highlighted (Fig. 4a). They show corona-like microstructures, developed during the firing process. Inside these calcite inclusions, acicular-shape crystals corresponding to CaAl-zeolite were identified (EDS results, Fig. 4b).
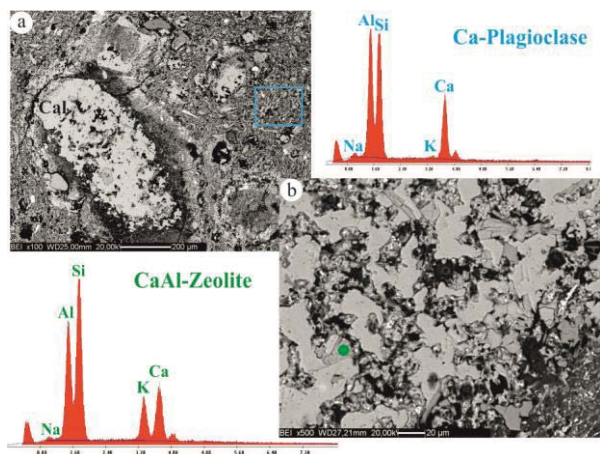

Fig. 4. SEM-BSE images and EDS analysis of the micromass of the pale yellowish pastes and the coarse calcite grains, with corona-like microstructures and CaAl-zeolite development within.

On the one side, Ca-rich microsites within such coarse calcite inclusions may foster gehlenite nucleation [8], that might be transformed into wairakite [9]. On the other, the abundant amorphous phase yielded by high-fired calcareous clays may foster zeolites formation [11], boosted in turn by the hydration of the amorphous phase and in presence of alkaline fluids [20]. As synthetized zeolites by alkali activation show a pozzolanic behavior and cementitious properties [21], it is suggested that CaAl-zeolite formation may improve the mechanical properties of these bricks, enhanced likewise by the high humid conditions of the areas in which they are placed. In the yellowish pastes, produced with coarse calcite inclusions that were partially preserved during firing, primary and secondary calcite coexist.

IV. CONCLUSIONS

The yellowish colour and the very similar mineralogical composition shown by the analysed bricks point out that they were produced according to analogous technologies, so the reuse of Late Antiquity bricks during Medieval times could be confirmed. The pale yellowish bricks reused to build up the Medieval Eastern wall of Saint Sigismund Chapel suffered a significant decay, largely due to the different environmental conditions that they were put through. This wall is exposed not only to an intense degree of insolation, but also to the changed climate conditions that may take place throughout the day on the city.

The coarse calcite inclusions in the pale yellowish bricks and the high humidity conditions measured at the Late Antiquity areas, have played an essential role in the formation of the zeolite hydration products. Thereby, Ca-rich microsites within such coarse calcite grains enhanced gehlenite nucleation, that were transformed into zeolites fostered in turn by the hydration of the amorphous phase. Even though the original location of the reused bricks studied is unknown, neither the environmental conditions that they were exposed to, it is suggested that high relative humidity conditions may favour the conservation of the pale yellowish bricks. The results achieved may be transfer to current ceramic industry to produce high-quality bricks especially suitable for the built heritage conservation/restoration placed at high humid environs.

V. ACKNOWLEDGMENTS

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