

Mineralogical and physical behaviour of solid bricks with additives

G. Cultrone ^{a,*}, E. Sebastián ^a, M.J. de la Torre ^b

^a *Departamento Mineralogía y Petrología, Universidad de Granada, Fuentenueva s/n, 18002 Granada, Spain*

^b *Departamento Geología, Universidad de Jaén, Alfonso X el sabio, 28-23700 Linares, Spain*

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Abstract

The paper studies the effect of additives such as calcite, dolomite and sodium chloride on the mineralogical–textural and physical–mechanical behaviour of solid bricks destined for use as new materials in the restoration of historic buildings. The behavioural differences between specimens with and without carbonates can be explained by the different evolution of texture and mineralogical composition developed during the firing process. Carbonates are shown to result in bricks with different mineralogy, depending on firing, but with a stable microstructure within a wide range of temperatures (800–1000 °C). This may be an advantage when manufacturing pottery but these pieces lack mechanical resistance to high temperatures. Salt partially modifies the mineralogy of the bricks, acting as a melting agent, especially at high firing temperatures, and giving rise to more resistant products which are suitable for restoration work.

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1. Introduction

Bricks are construction materials used since ancient times and currently display different states of deterioration in numerous historic buildings [1–4].

The use of additives in brick production is frequent and depends on the characteristics required. The main factors involved in manufacture are the type of raw material used and the firing temperature, both of which affect the quality of the final product.

This paper examines the effects of additives on the mineralogical–textural and physical–mechanical behaviour of solid bricks fired at different temperatures. The bricks were manufactured manually by the traditional method, using a clayey material from Guadix (Granada, Spain) as raw material. This area has a long tradition of ceramic manufacturing [5]. Different additives such as calcite, dolomite and sodium chloride were used in order to reproduce the technological characteristics of the old bricks. The addition of carbonates was preferred to the

use of natural clay rich in carbonates to minimize other factors (such as differences with respect to the mineralogy of the clays) which lead to differences between the final products. The conclusions drawn are thus applicable to the compounds studied as additives. The information obtained from this study is useful for the elaboration of new construction materials and the choice of the most suitable bricks for restoration.

These compounds are known to have been used since remote times to improve the quality of ceramic materials. In fact, the use of carbonates was known in the Roman times when marls were used in the production of “terra sigillata” [6,7]. Salt has been used by both ancient and modern civilizations to improve the quality and durability of the product. The Polynesians mixed salt-water with certain types of clay [8], but NaCl grains were also used by inland cultures, especially if the clay contained carbonated tempers [9]. According to some authors [10], even a low salt concentration can inhibit the phenomenon of “lime blowing” in the presence of grains of carbonates. In extreme cases, this phenomenon can result in the breakage of the pieces although less serious cases also result in greater alteration [5,11].

* Corresponding author. Tel.: +34-958-243340; fax: +34-958-243368.
E-mail address: cultrone@ugr.es (G. Cultrone).

2. Materials and methods

A raw material was employed in the manufacture of the bricks. This consisted of quartz (50%), phyllosilicates (40%, mainly illite, and, in smaller quantities, chlorite + kaolinite, smectites and paragonite) and feldspars (10%) [12]. The additives in powdered form ($\varnothing < 0.1$ mm) were calcite, dolomite and salt (10%, 10% and 5% by weight, respectively).

The bricks were fired in an electric oven and an oxidizing atmosphere at 800, 900 and 1000 °C. A constant temperature of 100 °C was maintained for 1 h followed by the higher temperature for 3 h. Heating velocity was $\approx 3^\circ\text{C}/\text{min}$.

The mineralogical and textural study of the bricks was carried out by powder X-ray diffraction (XRD), optical microscopy (OM) and scanning electron microscopy (SEM). A Philips PW 1710 diffractometer, equipped with an automatic slit was used for XRD under the following conditions: emission radiation = Cu $K\alpha$, voltage = 40 kV, intensity = 40 mA, goniometer speed = 0.1 $2\theta/\text{s}$. For OM a Zeiss Jenapol polarized light microscope was used, and, for SEM, a Zeiss DMS 950 with QX 2000 Microanalysis Link.

The analysis of the pore system of the bricks was carried out by studying its behaviour in different tests at the presence of water and in mercury injection porosimetry (MIP). In particular, free and forced absorption of water [13] and drying [14] tests were carried out. For these tests three specimens of each type were cut in the form of cubes with sides of 3 cm. The pore size of the bricks was determined using a Micromeritics Autopore III model 9410 porosimeter with a maximum pressure of

414 MPa, capable of measuring pores with diameter between 0.003 and 360 μm .

To analyse the mechanical behaviour of the bricks the velocity of propagation of ultrasonic waves and the compressive strength were measured in the specimens using a Steinkamp PB-5 ultrasound generator with transducers of 100 kHz and a Metro Com MI 30 press with a 3×10^5 kg capacity, respectively.

Finally, freeze–thaw tests were carried out (20 cycles of 24 h each) according to UNE 67-028-84 [15] to evaluate the degree of durability of the bricks with time and to study how the texture and pore system is affected by the water change from liquid to solid state.

3. Results and discussion

3.1. Mineralogy and texture

Table 1 shows the results of the semi-quantitative XRD analysis of the bricks with and without additives. The content of non-crystalline phases (m) was calculated following the method proposed by Huertas et al. [16], in which the quartz content is considered constant with increasing firing temperature. In this way the vitreous phase developed according to the temperature reached was quantified. The value of m stayed constant up to 1000 °C when large quantities of the vitreous phase appeared. In the specimen without additives all the phyllosilicates had disappeared at 800 °C except for the dehydrated phase of the illite (reflection at 10 Å), which decreased with increasing temperature, disappearing at temperatures >900 °C. Mullite was detected at this temperature, its concentration increasing with

Table 1

Result of XRD analysis of bricks fired between 800 and 1000 °C without additives (G) and with calcite (GC), dolomite (GD) and sodium chloride (GS)

	T (°C)	Qtz	Phy	Hem	Mul	Fs	Cal	Dol	Gh	m
G	800	****	***	*	–	*	–	–	–	**
	900	****	***	*	tr	*	–	–	–	**
	1000	****	–	**	tr	* ^a	–	–	–	***
GC	800	****	***	*	–	*	*	–	–	–
	900	****	***	*	–	*	*	–	–	tr
	1000	****	**	*	tr	* ^b	–	–	*	**
GD	800	****	****	–	–	*	*	tr	–	–
	900	****	***	*	–	*	tr	–	*	–
	1000	****	–	**	*	* ^b	–	–	**	**
GS	800	****	***	*	–	*	–	–	–	–
	900	****	***	*	–	*	–	–	–	*
	1000	****	–	**	*	* ^a	–	–	–	***

****, Very abundant; ***, abundant; **, medium; *, scarce; tr, traces; –, not detected.

Mineral symbols after Kretz [32]: Qtz, quartz; Phy, phyllosilicates; Hem, hematite; Mul, mullite; Fs, feldspar; Cal, calcite; Dol, dolomite; Gh, gehlenite; m , melt.

^a Is sanidine.

^b Is anorthite.

temperature. The quantities of quartz remained constant while the feldspar (ortose and/or microcline) evolved to sanidine. Another mineral phase which increased with temperature was haematite, suggesting the formation of iron oxides by recrystallisation from Fe liberated during decomposition of the phyllosilicates [17].

Analysis of the bricks with calcite showed the persistence of calcium carbonate up to 900 °C, although at very low concentrations. Lagzdina et al. [18] found that the disappearance of the carbonates could occur at 820 °C for dolomite and 890 °C for calcite, these values being similar to those found in the current study. Concentrations of the dehydrated phases of the phyllosilicates decreased with increasing temperature but were still present at 1000 °C. Contrary to what occurs in the bricks without additives, in these specimens, the presence of gehlenite can be related to that of haematite at very low concentrations. This takes place because, according to the observations of Maniatis et al. [19], the Fe^{3+} present in the specimens remains “trapped” in the structure of calcium silicates and aluminosilicates, as is the case of gehlenite, thus inhibiting the formation of haematite. The feldspar evolves into anorthite and the values of m are lower than in the bricks with additives.

In the bricks with dolomite a small quantity of calcite was detected in the specimens fired at 800 °C. This is due to the fact that, at this temperature, the decomposition of $CaMg(CO_3)_2$ into CaO and MgO may take place, and, on analysing the specimens, calcite is found because calcium oxide has the ability to recarbonate in a shorter time than the periclase [20]. The quantities of m formed

in the presence of dolomite were slightly higher than in the case of calcite, probably due to the decomposition of dolomite starting at a lower temperature than that of calcite. In this case both CaO and MgO act as melting agents [21]. For the same reason larger quantities of gehlenite are produced in the specimens.

The use of salt, even when added in small quantities (0.5%) favours the development of mullite, haematite and sanidine, no calcium aluminosilicates such as gehlenite being detected. This was expected since this mineral and the other calcium silicates (diopside, wollastonite) only appear where there is a high CaO concentration. The concentrations of m are also noteworthy, only slightly lower than in the specimens without additives. Although XRD did not reveal significant variations in the concentrations of the mineral phases and m , probably due to the limitations of this technique (the margin of error may be $\pm 5\%$ [22]), OM and SEM revealed a more vitrified texture in the presence of NaCl.

The temper of the specimens consisted of fragments of schists of around 1.5 mm or isolated quartz grains (Fig. 1(a)). In the bricks without additives the matrix was dark and became less birefringent (more vitreous) with increasing firing temperature (Fig. 1(b)). The phyllosilicates, which, at 800 °C still showed the optical characteristics of muscovite, were transformed into mullite. The replacement was considered complete at 1000 °C, maintaining the morphology of the muscovite (Fig. 1(c)). No significant differences were observed with respect to the bricks with additives. Only in the specimens with added carbonates could very small grains

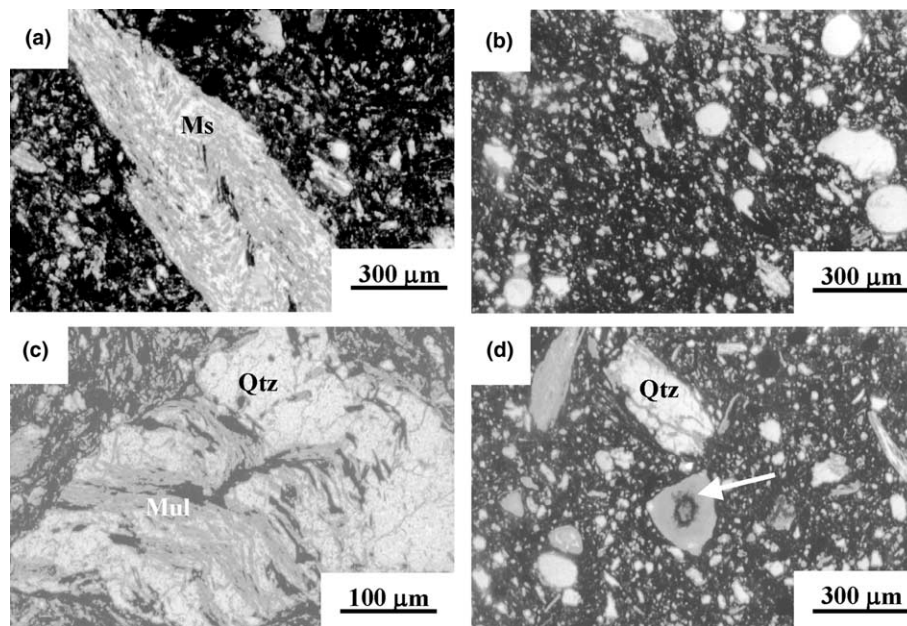


Fig. 1. Muscovite fold in brick with calcite (GC) and fired at 800 °C (a); vitrification of brick with NaCl (GS) fired at 1000 °C (b); total transformation of muscovite into mullite in a gneiss of a brick (G) fired at 1000 °C (c); grain of carbonate with darker edges in a brick with dolomite (GD) fired at 800 °C (d).

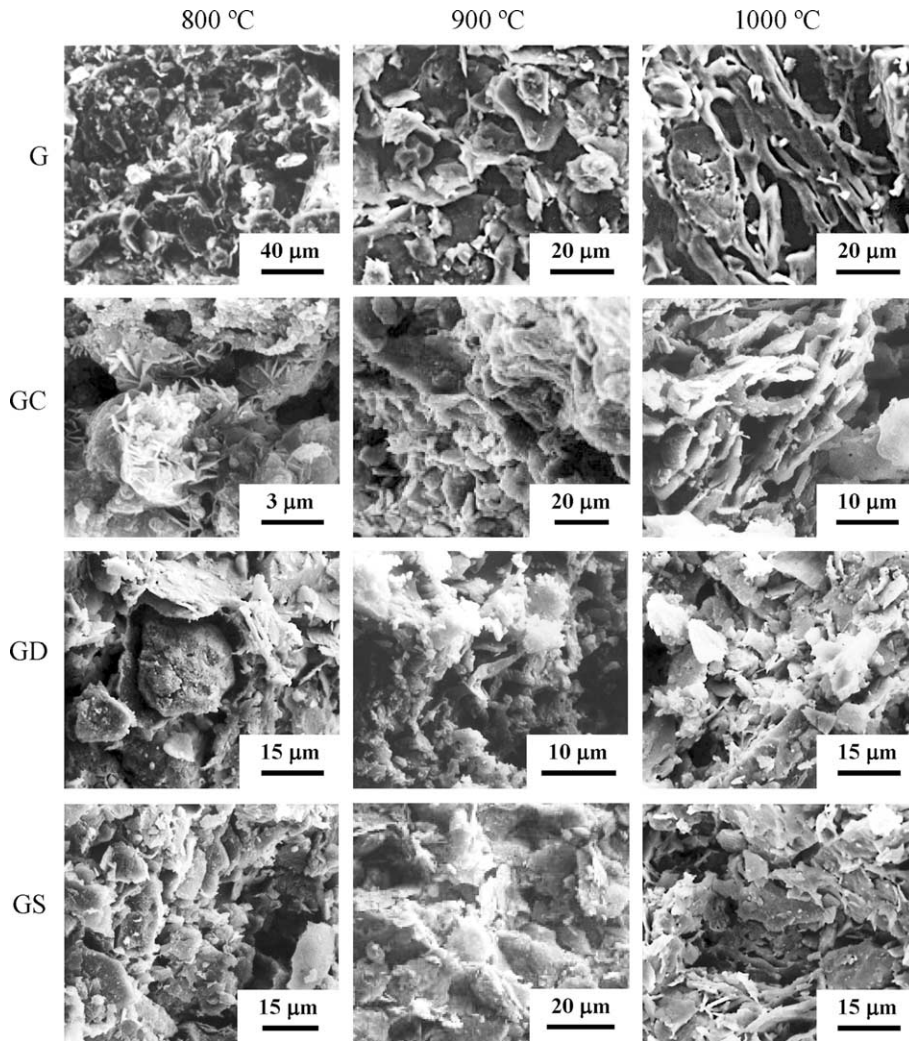


Fig. 2. SEM microphotographs of bricks without additives (G) and with calcite (GC), dolomite (GD) and sodium chloride (GS) fired at 800, 900 and 1000 °C.

partially transformed into other mineral phases be distinguished (Fig. 1(d)).

Using SEM (Fig. 2) it was observed that, at 800 °C, in the specimens without additives (G), the laminar character of the phyllosilicates was maintained although the muscovite crystals exhibited marked exfoliation along the basal planes due to dehydration. Interconnection between particles was limited. Vitrification was clearly observed in the specimens fired at 900–1000 °C. At 900 °C the phyllosilicates deformed and tended to join together; at 1000 °C the surface and shape of the grains became smoother and the pores took on an elliptical shape with smooth edges (“cellular structure”, [23]). At 800 °C, in the specimens with additives, the phyllosilicate layers lost their planar–parallel arrangement and adopted a rosette morphology. At 900 °C some differences started to appear: in the bricks with carbonates (GC and GD) and with NaCl (GS) still had an angular morphology and signs of vitrification were only partially observed. In the case of the carbonates, small grains of

portlandite originating from old crystals of calcite and/or dolomite were observed. At 1000 °C the bricks with salt were highly vitrified while the specimens with carbonates had not modified their texture. In this respect, Stimmell et al. [9] observed that common salt is capable to reduce the sintering temperature of the bricks. On the other hand, carbonates do not favour vitrification at high temperatures [24,25], but promote the development of a microtexture which is stable up to 1050 °C [26]. This is due to the fact that the silica and alumina proceeding mainly from destruction of the phyllosilicates are incorporated into the structure of new high temperature mineral phases such as gehlenite and thus impede the development of an aluminosilicate melt [27].

3.2. Hydric tests

The results of these tests indicate that in the specimens without additives a progressive reduction in water absorption capacity clearly takes place with increasing

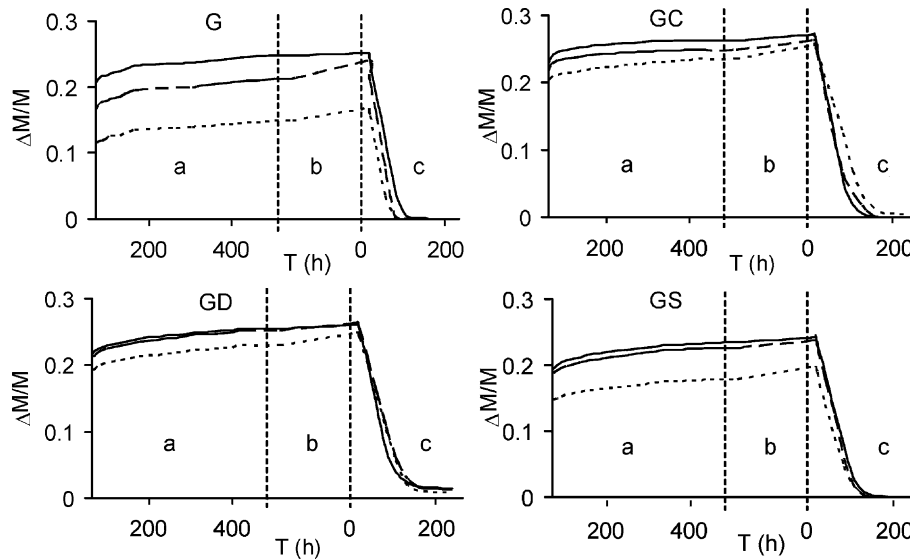


Fig. 3. Absorption (a), saturation under vacuum (b) and drying (c) diagrams of bricks without additives (G) and with calcite (GC), dolomite (GD) and sodium chloride (GS). Legend of firing temperatures: (---) 800 °C; (—) 900 °C; (.....) 1000 °C.

firing temperature. However, in the bricks with salt, and, above all, with carbonates, the differences in behaviour between specimens fired at different temperatures were minimal (Fig. 3). Only the bricks fired at 1000 °C clearly showed lower absorption values. Generally, the GS group was the most similar to the bricks without additives (G).

This behaviour is confirmed by the values in Table 2. Thus, although in all cases there was a decrease in the absorption capacity (A_1) of the bricks with increasing temperature, the values obtained for the specimens without additives (G) were similar only to the bricks treated with salt (GS): characterized by a minimal reduction of A_1 between 800 and 900 °C and much greater at 1000 °C ($A_1 \approx 15\%$ in G and 18% in GS). On the other hand, in the presence of carbonates there was no

notable evolution of absorption from 800 to 1000 °C (A_1 in GC went from 26% at 800 °C to 23% at 1000 °C and in GD from 25% to 23%).

The large decrease in absorption capacity in the G and GS specimens fired at 1000 °C is due to the loss of interconnection between the pores (A_x). This parameter is obtained by comparing the values of free (A_1) and forced (A_f) absorption and is directly related to the tortuous nature of the pore system of the material [5]. The highest values were those for G and GS fired at maximum temperature ($A_x \approx 11\%$ and 10% , respectively), as a result of the high degree of vitrification attained by these specimens, confirmed by the SEM study.

It should be noted that, at 800 and 900 °C, the lowest A_x values were recorded on bricks without additives and the highest on the specimens with carbonates. This may

Table 2

Hydric parameters of bricks without additives (G) and with calcite (GC), dolomite (GD) and sodium chloride (GS)

	T (°C)	A_1	A_f	A_x	C_a	D_i	S	P_o	D_A	D_R
G	800	24.84	25.14	1.19	0.097	0.079	88.16	39.28	1.58	2.62
	900	23.15	23.90	3.14	0.078	0.061	82.96	37.41	1.61	2.62
	1000	14.94	16.76	10.86	0.053	0.053	74.98	27.49	1.83	2.65
GC	800	26.13	27.16	3.79	0.110	0.108	91.49	42.08	1.55	2.68
	900	24.85	26.17	5.04	0.103	0.119	89.93	40.79	1.56	2.63
	1000	23.36	25.58	8.68	0.098	0.166	83.84	39.54	1.54	2.56
GD	800	25.31	26.10	3.03	0.097	0.168	88.41	40.33	1.56	2.62
	900	24.93	26.35	5.39	0.097	0.181	85.70	40.90	1.55	2.62
	1000	22.71	24.86	8.65	0.095	0.169	82.21	39.75	1.60	2.66
GS	800	23.41	24.25	3.46	0.079	0.130	85.96	38.49	1.59	2.58
	900	22.65	23.75	4.63	0.086	0.115	84.00	38.16	1.61	2.60
	1000	17.89	19.88	10.01	0.072	0.108	78.44	34.22	1.72	2.62

A_1 , Free absorption (%); A_f , forced absorption (%); A_x , degree of pore interconnection (%); C_a , absorption coefficient; D_i , drying index; S , saturation coefficient (%); P_o , open porosity (%); D_A , apparent density (g cm^{-3}); D_R , real density (g cm^{-3}).

be due to greater vitrification of GC and GD at low firing temperatures (although not observed with SEM) since the carbonates may act as melting agents [28] reducing the melting temperature of the bricks (eutectic CaO–SiO₂ [29]). However, at higher temperatures, as explained previously, it is difficult for carbonates to accentuate vitrification since crystallisation of the calcium and/or magnesium silicates is favoured.

For drying, behaviour varied according to the additive: in G and GS the bricks fired at low temperature took longer to dry, while for those with carbonates (GC and GD) the opposite took place. These differences can also be explained by the degree of vitrification attained by the bricks at 800, 900 or 1000 °C.

The saturation values (S) were very similar, decreasing with increasing temperature and ranging from 75% for G at 1000 °C to a maximum of 91% for GC at 800 °C.

The open porosity values (P_o) were around 40%, slightly higher for GC and GD but within the standard values for traditionally manufactured ceramic products [30]. The lowest values were reached by the most vitrified bricks (G and GS at 1000 °C). The density of the specimens varied from 2.58 to 2.68 g/cm³, being highest in the bricks fired at the highest temperatures.

3.3. Mercury injection porosimetry

Porosimetry revealed that pores with a radius of around 1 μm (Fig. 4) predominated in all the groups of

bricks. However, while in the case of the bricks without additives (G) a progressive migration of the curve towards larger pores took place, with increasing temperature, in the case of the specimens with carbonates (GC and GD) this evolution was virtually absent. This is due to the structure developed in these bricks being stable at temperatures between 800 and 1000 °C, as confirmed by SEM. On the other hand, the bricks prepared with salt showed, although not so clearly as G, an increase in the amount of larger pores with increasing firing temperature (Fig. 3). This agrees with the observations of Stimmell et al. [9]. According to these authors, the addition of even a small amount of salts to the bricks contributes to the development of larger pores to the detriment of the smaller ones, displacing the porometric curves towards pores with a larger radius. This tends to agree with SEM observations in that greater vitrification implies the development of relatively large rounded pores to the detriment of the original intergranular porosity which has an irregular morphology and lower diameter.

3.4. Ultrasonic and compression tests

All the specimens showed an increase in the ultrasonic waves propagation with increasing firing temperature (Fig. 5). In all cases the velocity was always higher perpendicular to the “side” (V_{P3}) and to the “end” (V_{P2}) of the bricks whereas the lowest values were measured perpendicular to the “face” (V_{P1}). The latter is the sur-

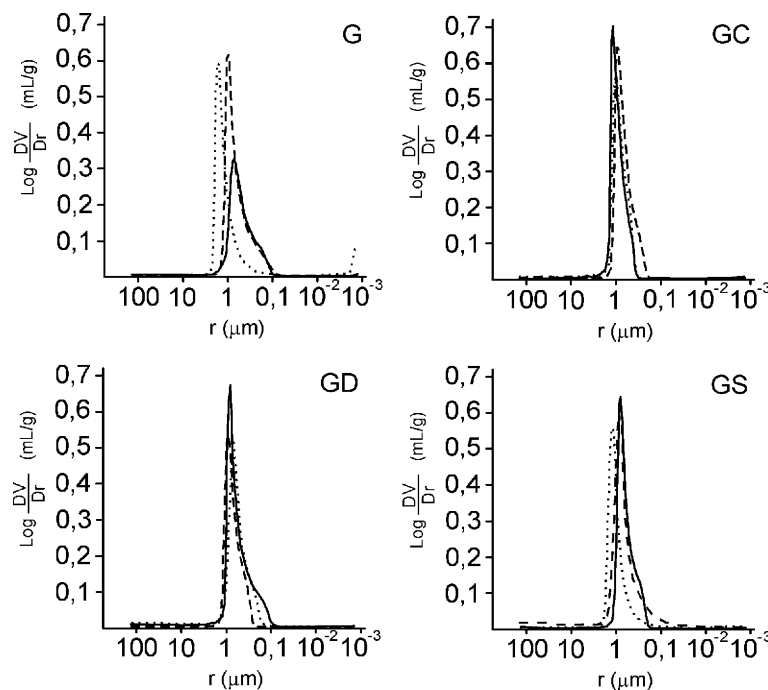


Fig. 4. Porometric curves of bricks without additives (G) and with calcite (GC), dolomite (GD) and sodium chloride (GS). Legend of firing temperatures: (---) 800 °C; (—) 900 °C; (.....) 1000 °C.

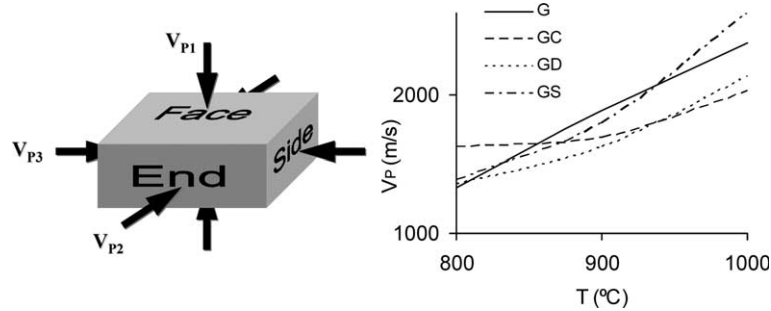


Fig. 5. Scheme of ultrasound measurement according to the faces of bricks and diagram of ultrasound wave velocity in bricks without additives (G) and with calcite (GC), dolomite (GD) and sodium chloride (GS). The diagram shows the mean velocity V_P (in m/s) with respect to the firing temperature (in °C).

face according to which a certain orientation of the layers of phyllosilicates is originated, thus slowing down the movement of the waves. The bricks without additives (G) showed the most regular evolution (Fig. 5), indicating progressive vitrification. The specimens with additives are characterized by a greater increase in the velocity of ultrasound at temperatures between 900 and 1000 °C as opposed to that between 800 and 900 °C. This is partly due to the development of new-formed denser mineral phases to the detriment of carbonates and/or phyllosilicates (gehlenite = 3.03 g/cm³, hematite = 5.30 g/cm³ and mullite = 3.05 g/cm³ on the one hand, and calcite = 2.71 g/cm³, dolomite = 2.84 g/cm³ and phyllosilicates (illite) = 2.75 g/cm³ on the other hand). The bricks prepared with sodium chloride (GS) are noteworthy for the high value of V_P at 1000 °C which confirms the melting nature of this salt in ceramic products.

Uniaxial compression test provides very similar results. Fig. 6 shows how the bricks resistance augments as the firing temperature increases. Notice the similarity of this diagram to the one of ultrasonic test (Fig. 5). The only difference is the higher strength of the bricks without additives fired at 1000 °C compared to specimens with NaCl (GS). Trend of the bricks with car-

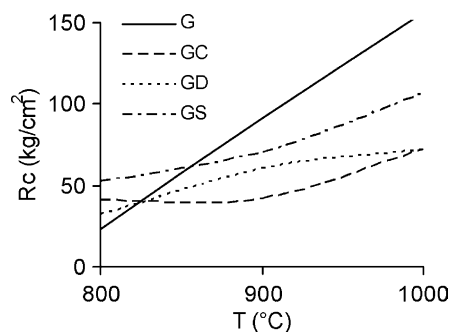


Fig. 6. Uniaxial compressive test evolution upon firing of bricks without additives (G) and with calcite (GC), dolomite (GD) and sodium chloride (GS). The diagram shows the compressive strength (in kg/cm²) with respect to the firing temperature (in °C).

bonates (GC and GD) confirms the behaviour illustrated by ultrasonic test.

3.5. Freeze–thaw tests

The behaviour of the bricks with and without additives was generally similar since all the specimens fired at low temperatures underwent notable deterioration as a result of freezing. Conditions improved with increasing firing temperature. In fact, the increase of vitreous phase in the bricks tends to reduce decay [31]. The bricks without additives (G) fired at 800 °C began to crumble on the ninth cycle with a total weight loss of 13.28% at the end of the test (Table 3). At 900 and 1000 °C virtually no variation in the behaviour of the bricks was noted and fragment loss was negligible or inexistent. In the bricks with additives resistance of the specimens improved with increasing temperature. Except for the bricks with carbonates (GD) fired at 1000 °C, which broke on cycle 24, the others resisted better with little damage after 30 cycles compared to the others (Fig. 7). All the groups experienced high weight loss, especially at 800 °C where up to 85% of the original material was lost, as in the case of GS (Table 3). However, this group evolved better with increasing temperature. At 1000 °C the bricks with salt (GS) showed the smallest fragment loss. The fact that GC and GD gave better results at 800 and 900 °C confirms the results on the interconnection of the pores (A_x , Table 2) obtained in the hydric tests, suggesting that these bricks attained a higher degree of vitrification with respect to those with sodium chloride.

Table 3
Weight loss (%) of bricks without additives (G) and with calcite (GC), dolomite (GD) and sodium chloride (GS) after freeze–thaw test

	800 °C	900 °C	1000 °C
G	13.3	0.9	0
GC	58.5	19.5	17.0
GD	22.0	17.0	23.5
GS	85.0	28.0	12.0

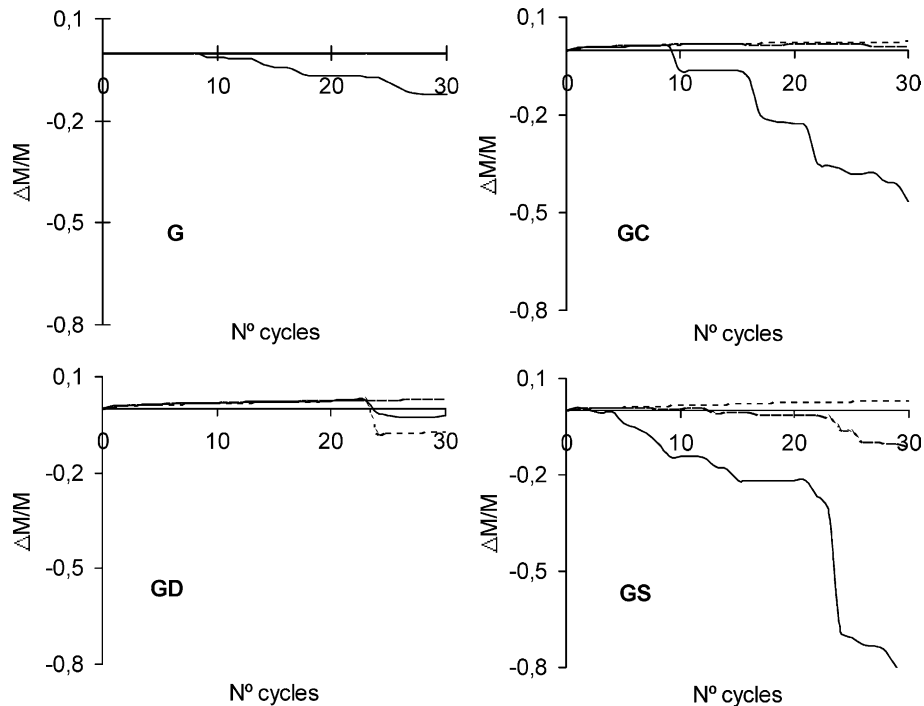


Fig. 7. Weight variation of bricks without additives (G) and with calcite (GC), dolomite (GD) and sodium chloride (GS) during freeze–thaw test. Legend of the firing temperatures: (---) 800 °C; (—) 900 °C; (·····) 1000 °C.

4. Conclusions

The results of this study show that the presence of additives in the clayey raw material, even in small quantities, significantly affects the behaviour and characteristics of the product. The greatest differences were observed when carbonates were added since these resulted in bricks with a higher degree of vitrification at low firing temperatures (800 and 900 °C). This greater vitrification should, in theory, improve the quality of the bricks, but is countered by the greater porosity and water absorption capacity. Consequently, the addition of carbonates may improve the technological properties of certain types of products, such as pottery, but not of construction materials.

In construction materials, particularly in those used for historic buildings, physical behaviour is the determining factor for the evaluation of their durability. The best results for hydric tests, ultrasound and accelerated ageing tests, used as a quality index for construction materials, corresponded to the bricks without additives or with salt and fired at 1000 °C since these are the most vitrified and thus the most resistant to physical and mechanical stress.

Therefore, the degree of vitrification and interconnection of pores are the most relevant parameters for predicting the durability of solid bricks in historic buildings. The results also show which factors affect these two parameters. As with the other factors, the degree of vitrification increases with increasing

temperature and reduces the connection between the pores. A more novel finding is that, regardless to temperature, the carbonates always have an influence since they increase absorption and interconnection of the pores. It is thus advisable to use raw materials with low carbonate content to obtain resistant bricks.

This study also shows the favourable effect of the addition of salt, which results in improved technological properties, equivalent to those of products without this additive and fired at higher temperatures.

The characteristics of the specimens with carbonates are summarized below:

- Microstructure is stable from low temperatures (800 °C) up to 1050 °C. This implies that increasing temperature has little effect on the product obtained, which has various technological advantages. Thus, a moderate error of overfiring does not reduce the quality of the product and is hardly noticed. This also saves on fuel since at low temperatures products of satisfactory quality are obtained.
- Crystalline structure with little development of the melted phase. This implies great textural anisotropy since gehlenite and other high temperature phases develop elongated crystalline habits. The anisotropy results in lower mechanical resistance and lower resistance to alteration agents such as ice or soluble salts.
- High porosity with small pore size due to the maintaining of the original texture of the grains and the

low development of the melt. These phenomena lead to greater decay.

The specimens without carbonates and those elaborated with salt showed the following characteristics:

- Great dependence on firing temperature. Consequently, the technological properties of the specimens fired at low temperatures are very different to those fired at high temperatures. This is advantageous since the characteristics of the product can be varied by changing this variable. However, it also means that an error in the calculation of the temperature will have a great impact on quality. The NaCl has a melting action, giving similar results to those obtained by an increase in temperature and thus saving energy.
- Vitreous texture with little development of high temperature phases. This results in lower anisotropy. The only prismatic phase produced is mullite but the great development of melt and the virtual disappearance of the original microstructure above 900 °C means that the final product is almost isotropic for ultrasound, leading to greater resistance to loading and to alteration agents.
- Rounded pores of large diameter resulting in lower susceptibility to ice and soluble salts. These bricks are more durable than those manufactured with carbonates.

These results lead to the conclusion that knowledge of the mechanisms of each of the factors involved in the manufacture of solid bricks permits the production of materials with preselected characteristics, suitable for every situation found in the conservation of historic buildings and the construction industry.

However, the selection of suitable materials for the restoration of historic buildings is not simple. The most durable material is not always the most suitable since it could divert the alteration agents towards the more sensitive original materials. In some cases, bricks rich in carbonates may be chosen for restoration in order that their high porosity acts as a “sponge” for the salts present in the medium, thus protecting the original bricks. However, greater knowledge of the properties of the materials will optimise conservation interventions.

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