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Technical quality of solid bricks made using clayey earth with added coffee grounds and fly ash

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ABSTRACT

This paper analyses the effects of the addition of organic (coffee grounds) and inorganic (fly ash) residues to a clayey soil rich in quartz and other silicates used as a raw material in brick production. To this end the mineralogy, texture, durability and physical and mechanical properties of solid bricks fired between 800 and 1100 °C were studied. The results show that as the firing temperature increased, the phyllosilicate content decreased and mullite appeared. The matrix became less birefringent due to gradual vitrification of the samples, especially after 950 °C. Vitrification resulted in more compact, less porous samples. The addition of residues did not affect the mineralogy, but it did alter certain physical parameters such as colour and porosity. The largest colour differences were detected after the addition of fly ash, which usually caused a whitish patina to develop on the surface of the fired bricks, while the highest porosity values were detected in bricks with coffee grounds, significantly reducing the bulk density. The increase in firing temperature improved the mechanical resistance and durability of all the bricks regardless of their composition.

1. Introduction

The European Union is faced with a serious problem as to what to do with the enormous amount of waste it produces. Current EU legislation seeks to establish a more sustainable model of revaluation and recycling of these waste products as an alternative to their disposal in landfills. The aim is that by the year 2025, 55% of all waste should be recycled, rising to 60% by 2030 (https://eur-lex.europa.eu/homepage.html).

One solution for the disposal of waste is to recycle it in the production of new building materials. A wide variety of organic and inorganic residues have been tested with a view to improving certain physical properties of these materials, focusing above all on mortars and concretes [36,29] rather than on bricks or other ceramic materials [59,60]. The successful use of waste products in brick manufacture would have two important benefits in that, in addition to recycling waste materials that would otherwise have to be dumped in landfills, it would also reduce the need for non-renewable raw materials such as clayey soils, thus contributing to the development of a circular economy [2].

In this research, the use of two waste products as additives in the manufacture of solid bricks was studied. One was organic (coffee grounds) and the other inorganic (fly ash). Coffee grounds are a common solid organic waste in homes, which is left over after coffee is brewed. Coffee is one of the most valuable primary products in the world, and the second most traded after oil. For each ton of coffee consumed, around 650 kg of residue is generated [37]. In 2020/2021, world coffee consumption was almost 10 million tons, which means that about 6.5 million tons of coffee grounds were produced (data from the International Coffee Organization, https://www.ico.org/). In Spain alone, in 2021 around 92,300 tons of this waste were produced. Tests were performed regarding the possible use of coffee grounds as fertilizer, but this was ruled out due to their acidity. At the moment, they are used as biomass in energy production [61] or as an adsorbent [39]. Little research has so far been done on the possible use of coffee grounds as an additive in brick production and with mixed results. Eliche Quesada et al. [17] demonstrated that the incorporation of 3% by weight of coffee grounds provided similar compressive strength to bricks without residues. Conversely, Sena da Fonseca et al. [49] and Muñoz Velasco et al. [34] observed that bricks with added coffee grounds had improved thermal insulation properties, although the increase in porosity caused by the calcination of this residue had a negative impact on their mechanical performance, which became worse as the residue content increased.

Fly ash is classified as Urban Solid Waste and is produced by the combustion of pulverized coal in power plants [27]. This coal typically

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contains carbon, together with mineral impurities such as clays, feldspars and quartz. During ignition in the furnace, the carbon burns while the mineral impurities melt in suspension and are transported out of the chamber by the exhaust gases, where they are caught by electrostatic filters [6]. Fly ash is the fine fraction of the non-combustible material. One of the problems of fly ash is its high specific surface value, which, in conjunction with its chemical composition, produces a high risk in terms of water contamination [3]. These particles are extremely fine and mostly glassy, which means that they have excellent pozzolanic properties. This is why it is widely used in the mortar and concrete industry in which it improves aspects such as durability and mechanical resistance, reducing greenhouse gas emissions produced during the manufacture of Clinker. If we compare the two selected residues, the use of fly ash in brick manufacture has received more attention from researchers than the use of coffee grounds. Some of the published papers centre on unfired products composed of a mixture of clayey earths and fly ash and stabilised with cementitious binders [45,22]. In recent research on fired bricks, it is surprising to note that in some studies the bricks containing fly ash obtained satisfactory results in tests on their physical parameters [26,15], while in others the results were poor [1,51].

These, sometimes contradictory, results led us to investigate whether the use of coffee grounds and fly ash can have beneficial or detrimental effects on brick production.

In this paper, we assess the possibility of adding either coffee grounds or fly ash to a raw material used to make bricks. We also assessed the possible advantages and disadvantages of firing them at three different temperatures and of following a different methodological approach. To this end, the chemistry and mineralogical composition of the bricks were analysed and the new phases that appeared during firing were identified. We also analysed the texture, pore system, colour, compactness and strength of the bricks and their durability against salt attack, in order to provide more detailed, more conclusive information regarding their behaviour. This study can provide further information about the behaviour of FCBs (eco-friendly fired clay bricks) [33] or eco-bricks, which help recycle materials that would otherwise accumulate in landfills.

2. Geology of the raw material outcrop area

The clayey soil used in the preparation and firing of the brick samples was provided by the "Cerámica Castillo Siles SL" brick factory in Víznar, Granada. The clay outcrops in the Guadix basin (Andalusia, Spain) in the central sector of the Betic Cordillera, and is in contact with two domains: Internal Zones (Alboran cortical domain) and External Zones (south-eastern Iberian margin). Sedimentary filling in this basin ranges from the Tortonian to the beginning of the Quaternary, with a marine sedimentation that evolves to continental [50]. The raw material comes from a local quarry (Lourdes quarry) with associated lithologies such as conglomerates, sandstones, red clays and carbonates. Gneisses, mica-schists and amphibolites from the Alpujarride complex can also be found in the surrounding area (Internal Zones of the Betic Cordillera).

3. Preparation and firing of brick samples

The first stage was to break up the clay lumps and sieve the raw material to discard any fragments larger than 1.5 mm. We then had to decide how much residue to add. If the goal is to reuse as much residue as possible, it should make up a high percentage of the mix used to make the bricks. Clearly, this high percentage must not affect the consistency and quality of the bricks. When investigating this question, Abbas et al. [1] found that the bricks made with added fly ash were not as strong as the bricks with no additives and that they became progressively weaker as the amount of ash increased from 0 to 25% by weight. Sena da Fonseca et al. [49] observed a similar trend in the mechanical performance of bricks with the addition of increasing percentages of coffee grounds up to 20% by weight. The addition of just 5% of waste caused a decline in strength decay of over 30%. In this research, we decided to add 20% by weight of fly ash and 10% by weight of coffee grounds in order to try to obtain resistant, durable bricks. The bricks were fired at three different temperatures for comparison purposes. A control group of bricks was prepared with the same raw material, but with no added residues. The decision to use a smaller percentage of coffee grounds (10% by weight) than of fly ash was based on the fact that coffee grounds are very light. Adding 20% by weight of coffee grounds would have required an excessively high volume of this residue and the resulting bricks would have been very brittle. The fly ash was supplied by the Los Barrios Thermal Power Plant (Cádiz, Spain) and the coffee grounds came from the coffee shop at the Faculty of Science (University of Granada). The samples were prepared by hand because the brick factory that supplied the raw material produces its own bricks both by extrusion and by hand. The latter are often used in the cladding of houses and in the restoration of architectural heritage. The clayey earth with and without residues was put in a rubber basket and kneaded by hand for about 20 min, gradually adding the kneading water and breaking up any clay lumps that might be present. The addition of residues, especially the coffee grounds, required more water to be added to the mix to obtain a mouldable mass. In the case of fly ash, 35 vol% more water was used, while with coffee grounds, this figure was much higher (89 vol%), due to the intrinsic properties of this residue. Both residues were added as is, i.e. no grinding or sieving was required prior to mixing them with the clay. Once the right consistency had been obtained, the mix was placed into a wooden mould measuring 16 × 12 × 4 cm. The mix was then pressed down by hand until the mould was completely full and compacted,. Any excess was removed with a ruler, leaving smooth flat surfaces. After half an hour it was demoulded and cubic bricks measuring approximately 4 × 4 × 4 cm were cut with a stretched cotton thread and were left to dry in the laboratory for a week. The bricks were then fired in a Herotec CR-35 electric oven in an oxidizing atmosphere at 800, 950 and 1100 °C. In this way, the changes that occur in the bricks over a 300 °C range in terms of mineralogy, degree of vitrification, porous system, compactness, colour and durability were assessed. Table 1 shows the acronym assigned to each type of brick based on its composition and firing temperature. The samples were heated gradually, increasing the temperature by between 6 and 8 °C per minute depending on whether or not coffee grounds were added (Table 1). It seems that the combustion of this organic residue acted as a catalyst for the firing process, so accelerating the firing times. In this regard, Dondi et al. [14] observed that various organic wastes can generate significant amounts of heat.

Table 1
Acronym assigned to each brick group based on the type of additive and the firing temperature. The rate at which the temperature was increased during the firing of each brick (in °C/min) is indicated in brackets.

Additive	800 °C	950 °C	1100 °C
none	G800 (7.5)	G950 (6.3)	G1100 (6.4)
Coffee grounds	Gcg800 (8.1)	Gcg950 (7.5)	Gcg1100 (7.6)
Fly ash	Gfa800 (7.3)	Gfa950 (6.3)	Gfa1100 (6.7)

Once the maximum temperature was reached, it was maintained for three hours. Then, the oven was switched off, although the samples were left inside until the next day. This allowed the bricks to cool slowly, so ensuring that they did not crack due to the β-to-α quartz transition at 573 °C [25]. Once the bricks were removed from the oven, they were immersed in water to prevent "lime blowing", a phenomenon that occurs when calcium oxide grains present in the mix are hydrated [28].

4. Methodology

4.1. Analysis of the clayey material and additives

The particle size of the different raw materials (clayey material from

Table 2
Chemical analysis of major oxides (in wt.%) and trace elements (in ppm) in the raw material from Guadix (G) and the fly ash (fa). LOI stands for loss on ignition.

	SiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	LOI
G	58.08	18.85	7.78	0.08	1.28	1.69	0.81	2.89	0.95	0.13	8.02
fa	55.37	17.18	6.61	0.06	1.62	7.12	0.87	1.96	0.77	0.18	5.66
	Zr	Sr	Cr	Ba	Ni	Pb	Rb	V	Y	Zn	
G	302	146	108	404	49	39	138	106	46	91	
fa	177	270	123	662	57	37	112	174	36	176	

Guadix, coffee grounds and fly ash) was measured with a Malvern Instruments Matersizer 2000LF laser meter that analyses particles in the range 0.02 μm − 1.5 mm. The chemistry (major and trace element) of the clay and the fly ash was analysed by X-ray fluorescence (XRF) using a PANalytical Zetium compact spectrometer. 7 g of sample was milled to powder in an agate mortar and analysed.

The mineralogy of the raw material was determined by powder X-ray diffraction (PXRD) using a PANanalytical X'Pert PRO diffractometer, under the following working conditions: CuKα radiation (λ = 1.5405 Å), voltage 45 kV, intensity 40 mA, a scan angle 4-70° and goniometer speed of 0.1 2θ s^{-1}. The HighScore 4.8 computer program (Malvern Panalytical) was used to interpret the diffractograms.

Thermogravimetry (TG) and Differential Scanning Calorimetry (DSC) were used to determine the weight loss in the clayey material due to the possible combustion of organic matter, dehydration and dehydroxylation phenomena and CO_2 release due to the increase in temperature, so as to complete the information provided by PXRD. Analyses were carried out using a Mettler-Toledo TGA/DSC1. Approximately 40 mg of sample was deposited in an aluminium crucible with a heating rate of 20 °C/min and a temperature range of 25–950 °C.

4.2. Analysis of fired bricks

The identification of mineral phases in bricks with and without additives fired at 800, 950 and 1100 °C was carried out by powder X-ray diffraction (PXRD), using the same apparatus and the same procedure mentioned above.

The changes in the mineralogy and texture of bricks that took place in line with the increase in firing temperature were observed by polarized optical microscopy (POM) using a Carl Zeiss Jenapol-U microscope coupled with a Nikon D7000 digital microphotography unit. One thin section per brick type was prepared and observed under transmitted light and the images were saved in plane- and cross-polarized light.

Hydric tests provide information on the absorption and drying capacity of bricks over time. They also shed light on how the composition and firing temperature of the bricks can influence the water flow inside them. Free (A_b) and forced water absorption (A_f) and drying (Di) were measured on three samples per brick type under controlled thermo-hygrometric conditions (22 °C and 35% relative humidity) according to the UNE-EN 13755 [54] and NORMAL 29/88 [35] standards, respectively. These tests allowed to calculate the degree of pore interconnection (Ax [9], saturation coefficient (S), apparent and real densities (ρ_a and ρ_r) and open porosity (P_o) [42].

The study of the porous system was completed by mercury intrusion porosimetry (MIP) to define the pore size distribution of bricks within the range 0.002–200 μm. Apparent and real densities (ρ_{aMIP} and ρ_{rMIP}), specific surface area (SSA) and open porosity (P_{oMIP}) were also calculated. A Micromeritics Autopore IV 9500 porosimeter was used to analyse one fragment per brick type of about 1 cm^3 previously dried in an oven at 70 °C for 8 h.

Ultrasound is a non-destructive technique that helps evaluate the compactness of materials and their anisotropy due to the orientation of the grains and the presence of pores and fissures [18]. A Controls 58-E4800 ultrasonic pulse velocity tester was used together with transducers with a frequency of 54 kHz on three dry cubic samples per brick type, in accordance with the ASTM D2845 [4] standard. The structural anisotropy (ΔM) was calculated as follows:

$$\Delta M = 1 - \frac{2V_{P1}}{V_{P2} + V_{P3}} \times 100 \quad (1)$$

where V_{P1} is the velocity measured perpendicularly to the compaction plane of the clayey earth in the wooden mould, and V_{P2} and V_{P3} are the velocities measured parallel to it.

The mechanical resistance of bricks was quantified in a uniaxial compression test using a Matest E181 press that can generate a maximum load of 250 kN. The test was carried out on three cubic bricks per type according to the UNE-EN 1926 [52] standard. The surfaces of the cubes were previously smoothed with a cutting disk in order to obtain perfectly flat, parallel surfaces. The strength was measured perpendicular to the compaction plane of the raw mixture in the wooden box.

Colorimetry is another non-destructive technique used here to quantify the colour of the samples and possible differences between them. Three measurements were performed per brick type using a portable spectrophotometer Konica Minolta CM-700d, according to the UNE-EN 15886 [55] standard. A CIE D65 illuminant with a colour temperature of 6504 K was used to measure the lightness (L*), chromatic coordinates (a* and b*), chroma (C*) and hue (h°) in the 400–700 nm wavelength range. A pulsed xenon lamp illuminated a circular area of bricks with a diameter of 8 mm (10° vision angle). The light was measured in SCI and SCE modes. The colour difference between the bricks without additives and those with added coffee grounds or added fly ash (ΔE) was calculated as follows:

$$\Delta E = \sqrt{(L_1^* - L_2^*)^2 + (a_1^* - a_2^*)^2 + (b_1^* - b_2^*)^2} \quad (2)$$

where L_1^*, a_1^*, b_1^* correspond to the lightness and chromaticity of the bricks made without additive and L_2^*, a_2^*, b_2^* to those made with additives.

Finally, 15 salt crystallization cycles were carried out according to the UNE-EN 12370 [53] standard to assess the damage caused by soluble salts when they crystallize in the pores and fissures in the bricks. Three samples per brick type were immersed in a 14% $Na_2SO_4 \cdot 10H_2O$ (mirabilite) solution. The phase change from anhydrous (thenardite) to decahydrated (mirabilite) can produce a crystallization pressure of 14 MPa in confined spaces, which can cause the materials to decay [19]. Decay was monitored after each cycle (1 cycle = 24 h) by visual inspection and weight measurement.

In the physical tests conducted as part of this research, the RILEM, EN, ASTM and NORMAL standards were followed. Due to the size of the wooden moulds used in this research, we had to deviate slightly from these standards. Instead of bricks with a 5 (or 7) cm-edge, our samples had a shorter 4 cm-edge. Similarly, although in the standard for the strength test, 6 samples were recommended, we only used 3. This was due to the fact that a limited number of samples were available for a large set of analyses.

5. Results and discussion

5.1. Raw material and additives

Table 2 shows the results of the chemical analysis (major oxides and trace elements) of the raw material from Guadix and the fly ash. Guadix

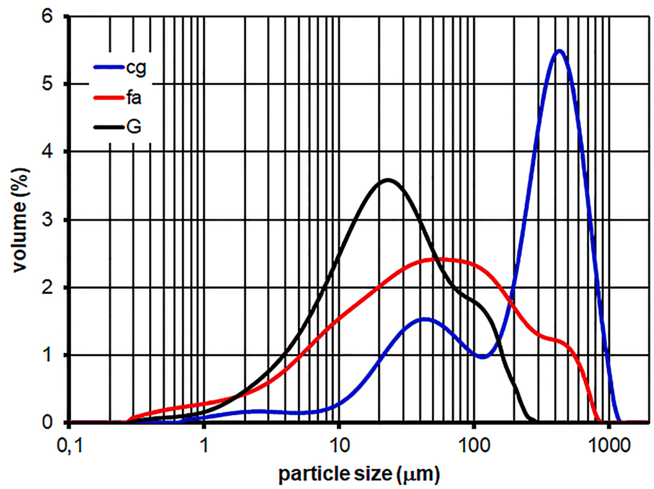

Fig. 1. Grain-size distribution curves for the clayey material from Guadix (G), the coffee grounds (cg) and the fly ash (fa).

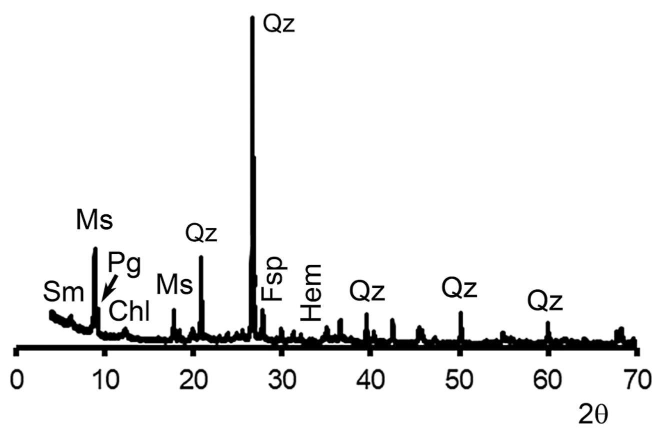

Fig. 2. Powder X-ray diffraction (PXRD) diagram for the raw material from Guadix. Legend: Qz = quartz; Ms = illite/muscovite; Sme = smectite; Chl = chlorite + kaolinite; Pg = paragonite; Fsp = feldspar *s.l.*; Hem = hematite. Mineral abbreviations after Whitney and Evans [57].

(G) is mainly composed of silica and alumina and smaller amounts (in decreasing order) of iron, potassium and calcium. Silica and alumina are also major components of fly ash (fa). Iron and calcium are also abundant, the latter in higher concentrations than in the raw material from Guadix.

The loss on ignition (LOI) is slightly higher in Guadix (8%) and may be related to the combustion of organic matter and the dehydroxylation of phyllosilicates, while LOI in fly ash (5.7%) may be due to the decomposition of carbonates, given the CaO content detected by XRF.

As regards the content in trace elements, this is usually higher in fly ash, where Ba and Sr predominate, while the most common trace element in Guadix is Zr. This may be due to the presence of detrital zircons, which are washed down from Sierra Nevada into the Guadix basin [46,23].

The granulometric curves for the clay, the coffee grounds and the fly ash show bimodal distribution in which one of the two families is much more developed than the other (Fig. 1). The highest occurrence of particles in Guadix (G) is observed at around 20 µm with a second less abundant family at 150 µm. In coffee grounds (cg), the highest particle occurrence is at around 400 µm with a second family at 50 µm. In the fly ash (fa), the main pore family is observed at around 60 µm and there is another at 400 µm.

In mineralogical terms, the raw material from Guadix is composed of quartz, phyllosilicates, feldspars *s.l.* and hematite, the latter in traces. Of the phyllosilicates, illite/muscovite is the most abundant phase, while smectites, chlorite, kaolinite and paragonite are detected in low concentrations (Fig. 2).

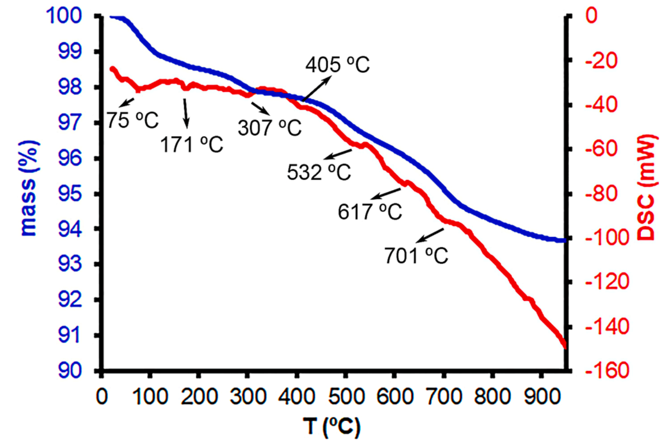

Fig. 3. Thermogravimetry (TG, in blue) and Differential Scanning Calorimetry (DSC, in red) curves for the raw material from Guadix.

Fig. 3 shows the results of the thermogravimetric (TG) and differential scanning calorimetry (DSC) analysis of the raw material from Guadix. A first endothermic peak was observed at 75 °C in both the TG and DSC curves, which indicates the loss of hygroscopic water present in the sample. Two more peaks were observed at 171 and 307 °C. These correspond to the combustion and decomposition of labile organic matter [21] present in the clay soil. Three peaks were identified at 405, 532 and 617 °C, due to the dehydroxylation of phyllosilicates. Phyllosilicates with low crystallinity, such as smectites, lose their OH^- at lower temperatures (i.e., at around 400 °C), while the second peak may be linked to the decomposition of chlorite and kaolinite. Those with a high degree of crystallinity such as muscovite and paragonite dehydroxylate at about 600 °C [8].

From 700 °C the TG curve shows a slight, albeit continuous, decrease with a weight loss of little more than 1% due to the loss of further OH^- from muscovite-type phyllosilicates [43].

Table 3
Mineralogical composition of fired bricks by PXRD. Legend: Qz = quartz; Ms = illite/muscovite; Fsp = feldspar; Hem = hematite; Mul = mullite. *** = abundant; ** = present; * = scarce; tr = in traces. Mineral abbreviations after Whitney and Evans [57].

	Qz	Ms	Fsp	Hem	Mul
G800	***	**	*		
G950	***	*	*	*	
G1100	***			*	*
Gcg800	***	**	*		
Gcg950	***	*	*	tr	
Gcg1100	***			*	*
Gfa800	***	**	*		
Gfa950	***	*	*	*	
Gfa1100	***		*	*	*

5.2. Fired bricks

5.2.1. Mineralogy and texture

Table 3 shows the PXRD results for the mineralogy of the bricks without additives and of those with added coffee grounds or fly ash and the changes that take place in line with increasing firing temperature. These transformations are quite similar to those that occur during major thermal metamorphism, although on a much smaller scale [20].

At 800 °C the most common mineral phase is quartz, while

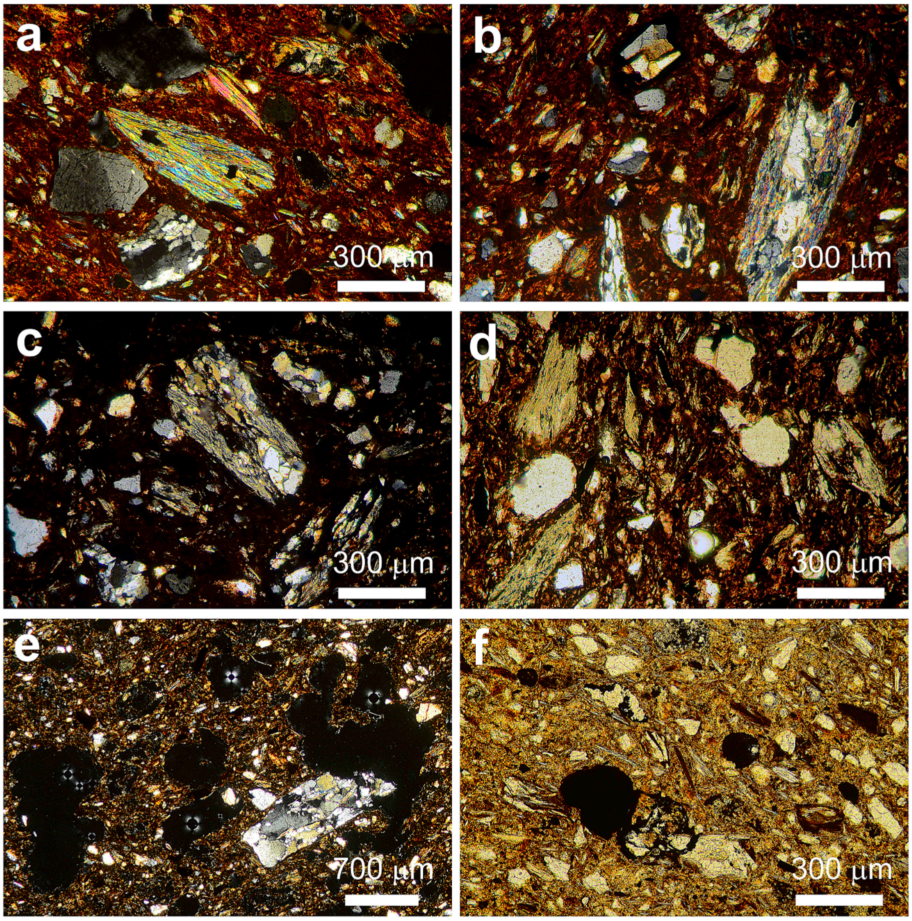

Fig. 4. Polarized optical microscopy (POM) images of: a) mica schist with second order green–blue interference colour and quartz grains with undulose extinction and a mosaic texture in a reddish matrix in the G800 brick (cross-polarized light); b) gneiss fragment with still birefringent muscovite-type sheets in the G950 brick (cross-polarized light); c) view of G1100 brick where the matrix has turned dark and phyllosilicates have lost their typical birefringence (cross-polarized light); d) pore morphology in the G1100 brick (plane-polarized light); e) texture of the Gcg800 brick with the presence of large pores (cross-polarized light); f) texture of the Gfa800 brick in which opaque, rounded-to-oval fly ash particles can be seen (plane-polarized light).

phyllosilicates and feldspars are also detected. While the quartz remains more or less stable at the three firing temperatures, of the phyllosilicates identified in the raw material, only the dehydroxylated phase of the illite/muscovite remains. This mineral decreases in concentration at 950 °C and disappears at 1100 °C, when mullite appears. According to Rodriguez Navarro et al. [43] and Cultrone and Carrillo Rosua [8] the illite/muscovite undergoes topotactic replacement by mullite.

Small amounts of K-feldspar could still be detected at 800 and 950 °C although it was not observed at 1100 °C, except in bricks with added fly ash. The fact that there is little or no feldspar content in the bricks fired at high temperature is due to the fact that this tectosilicate does not have time to develop its crystalline structure (sanidine) and it remains as amorphous phase [10]. The firing of bricks also favours the crystallization of hematite, a process enhanced by the breakdown of the phyllosilicates [38].

The addition of the residues did not lead to the appearance of any new mineral phases apart from those already detected in the bricks made without additives (Table 3).

Quartz grains are easy to recognize under polarized optical microscopy. It is the most common mineral and appears in the form of isolated grains with angular morphology and undulating extinction and as a component of gneiss and, less frequently, mica schist fragments (Fig. 4a). Muscovite crystals reach second order interference colours in bricks fired at 800 °C and 950 °C (Fig. 4b), but at 1100 °C they lose their

Table 4
Hydric and MIP parameters of fired bricks with and without additives. Legend: A_b = free water absorption (%); A_f = forced water absorption (%); Ax = degree of pore interconnection; S = saturation coefficient (%); Di = drying index; P_o and P_{oMIP} = open porosity (%, the second determined by MIP); ρ_a and ρ_{aMIP} = apparent density (g cm^{-3}, the second determined by MIP); ρ_r and ρ_{rMIP} = real density (g cm^{-3}, the second determined by MIP); SSA = specific surface area (m^2/g, determined by MIP); r_{max} = radius pore size at the maximum peak in each porometric curve (µm). Brick acronyms as in Table 1.

	G800	G950	G1100	Gcg800	Gcg950	Gcg1100	Gfa800	Gfa950	Gfa1100
A_b	21.77	20.41	10.06	38.91	35.46	21.24	25.61	24.88	15.26
A_f	22.09	21.00	12.74	45.92	43.18	30.56	26.07	25.72	17.50
Ax	1.45	2.77	21.11	15.25	17.90	30.84	1.76	3.26	12.88
S	88.55	86.30	65.97	73.83	70.61	55.21	90.27	88.34	75.19
Di	0.91	0.92	0.93	0.88	0.88	0.89	0.90	0.86	0.91
P_o	35.82	34.86	24.76	53.72	52.31	40.03	39.62	39.52	31.03
ρ_a	1.62	1.66	1.95	1.17	1.21	1.31	1.52	1.54	1.77
ρ_r	2.53	2.55	2.59	2.53	2.54	2.46	2.52	2.54	2.57
SSA	9.27	9.14	1.72	14.13	12.31	13.40	13.03	7.25	9.56
r_{max}	0.9	1.2	2.3	1.2	1.8	18.2	0.8	1.2	2.6
P_{oMIP}	35.57	38.55	29.00	53.87	51.45	46.84	40.98	39.81	35.33
ρ_{aMIP}	1.76	1.65	1.92	1.22	1.28	1.36	1.57	1.61	1.72
ρ_{rMIP}	2.69	2.68	2.70	2.65	2.63	2.55	2.66	2.64	2.65

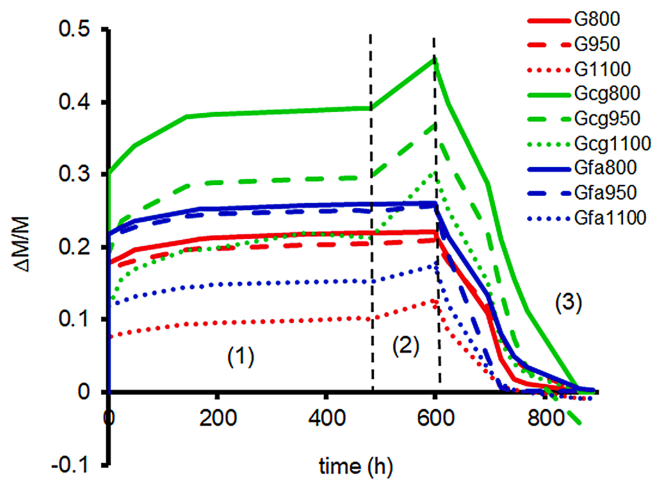

Fig. 5. Free absorption, forced absorption (under vacuum, 2) and drying curves (3) for the bricks without additives and with added coffee grounds and fly ash fired at 800, 950 and 1100 °C. Weight variation (ΔM/M) over time (in hours). Brick acronyms as in Table 1.

birefringence and turn white (Fig. 4c). The change in the birefringence of muscovite is due to the replacement of this mineral by mullite, so confirming PXRD analysis. The matrix of the bricks becomes darker and less birefringent as the firing temperature increases due to the gradual vitrification of the samples (Fig. 4c). Another effect of the firing process was the change in the morphology of the pores from angular to rounded (Fig. 4d). The addition of coffee grounds produces an increase in porosity, leaving voids where the organic particles were once present (Fig. 4e), while in the bricks made with added fly ash, this residue is easily identifiable as scattered spheres in the matrix of the bricks (Fig. 4f).

5.2.2. *Pore system*

Hydric tests revealed that the bricks fired at the highest temperature (1100 °C) absorb the least water (A_b, Table 4 and Fig. 5), while the bricks fired at 950 °C absorb less water than those fired at 800 °C.

Similar behaviour was also observed during the forced (under vacuum) absorption of water (A_f). The addition of residues produces bricks with a greater capacity to absorb water (Fig. 5).

In particular, the samples made with coffee grounds (Gcg) absorbed most water thanks to the appearance of new pores within the bricks after the combustion of the organic matter (part 1 of Fig. 5), as demonstrated by the observations under the microscope (Fig. 4e). The samples made with fly ash (Gfa) absorb more water than the bricks with no additives, although in this case the absorption values are clearly lower than those for the bricks made with coffee grounds. The greatest difference in the degree of absorption is usually observed between 950 and 1100 °C rather than between 800 and 950 °C. This suggests that the vitrification process becomes more intense from 950 °C onwards. The vitrification of the samples between 950 and 1100 °C, on the one hand, and the addition of coffee grounds, on the other, are responsible for a worsening of the degree of pore interconnection (Ax, Table 4 and part 2 of Fig. 5). Indeed, the highest Ax values were recorded in the samples fired at 1100 °C, and the highest of all (i.e. the worst interconnection) in Gcg1100. Ax values are inversely related to the saturation coefficient (S, Table 4): the higher the Ax, the lower the S. This result is logical given that in bricks with poor interconnection between the pores, it is more difficult for water to circulate, so the bricks become less saturated.

The drying index (Di, Table 4) shows quite similar results for all the samples and, therefore, similar drying rates. Within each group of bricks, the highest Di values (slower drying) were observed in the bricks

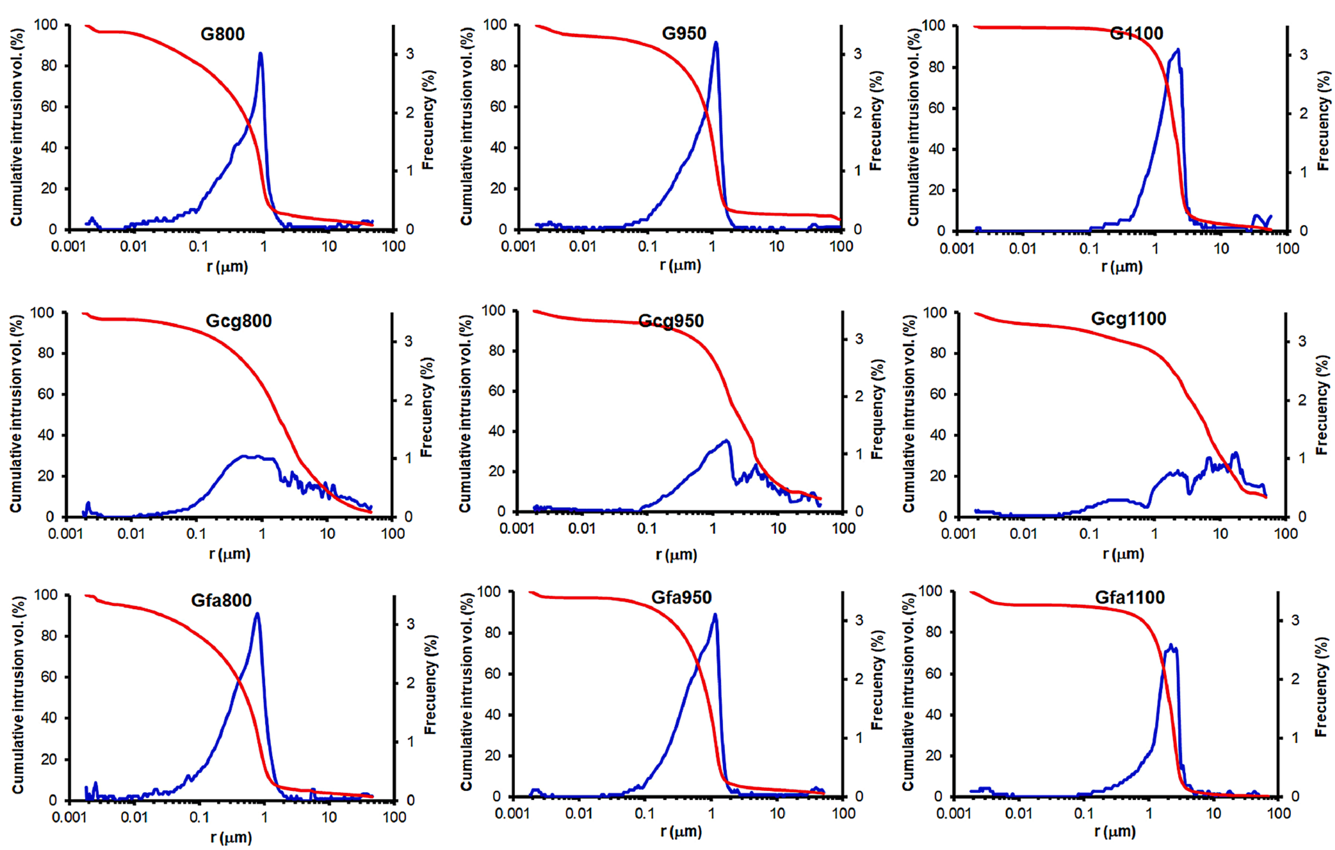

Fig. 6. Pore radius (in μm) distribution (blue) and cumulative curves (red) of bricks made with and without additives, as determined by mercury intrusion porosimetry (MIP). Brick acronyms as in Table 1.

Table 5
Compactness and strength of bricks made with and without additives determined by ultrasound and uniaxial compression tests. V_{P1}, V_{P2} and V_{P3} = Ultrasonic velocities measured along the three orthogonal brick surfaces (m/s). V_{P1} is the P wave velocity perpendicular to the compaction plane of the raw material, V_{P2} and V_{P3} are the P wave velocities parallel to it; $\overline{V_P}$ = mean of the P wave velocity (m/s). ΔM = structural anisotropy (%); CS = compressive strength (MPa). Brick acronyms as in Table 1.

	V_{P1}	V_{P2}	V_{P3}	$\overline{V_P}$	ΔM	CS
G800	962	1246	1230	1146	22.08	6.26
G950	1383	1756	1637	1592	18.50	11.57
G1100	2346	2660	2758	2588	13.20	34.20
Gcg800	809	1006	1088	967	22.42	2.47
Gcg950	1180	1469	1431	1360	18.71	4.86
Gcg1100	2132	2366	2291	2263	8.40	19.93
Gfa800	821	1081	1042	981	22.58	4.32
Gfa950	1125	1438	1495	1353	22.95	9.77
Gfa1100	2145	2427	2449	2340	12.04	28.48

fired at 1100 °C. This is due to their high level of vitrification, which hampers water's exit from the brick.

The most porous samples (P_o, Table 4) are those made with coffee grounds, in which empty spaces occupy over 50% of total volume, making these bricks considerably lighter than the others. A significant decrease in porosity is observed as the firing temperature increases, especially from 950 to 1100 °C. This confirms that most of the vitrification process took place within this temperature range. The samples with the lowest apparent density values (ρ_a, Table 4) are those containing coffee grounds, which show much lower values than the samples with no additives or with added fly ash and fired at the same temperature. The real density values (ρ_r, Table 4) are similar for all the samples, as this depends on the mineralogy of the bricks, which varied little, in line with PXRD results (Table 3).

The hydric behaviour of the studied bricks is in line with that of other handmade bricks fired between 800 and 1100 °C to which various organic and inorganic additives were added [44,16]. It must be said that it is quite difficult to compare the physical behaviour of handmade bricks with those made by extrusion or pressing. This is because the extrusion or pressing machines require less kneading water and produce more compact bricks than those made by hand [7,48]. This means that the moulding process is another variable that significantly affects the physical behaviour of the bricks. In general, pressed bricks made with the addition of organic residues such as, for example, sawdust, tobacco, tea and Kraft pulp have slightly lower water absorption and porosity values than Gcg bricks [5,12,13]. Other studies of the use of inorganic residues as additives in the production of extruded and pressed bricks observed higher or lower hydric values compared to Gfa samples depending on the properties of each additive (for example, polystyrene, glass, iron tailings and diatomite mud) [56,58,30,24].

As regards the mercury intrusion porosimetry (MIP) study, the bricks made with no additives showed unimodal pore size distribution (Fig. 6). In G800, most of the pores fall within the 0.1–1 μm size range with a maximum peak at 0.9 μm. This peak tends to shift towards larger sizes as firing temperature increases (1.2 μm at 950 °C and 2.3 μm at 1100 °C, r_{max}, Table 4). This suggests that at 950 °C and, above all, at 1100 °C, small pores coalesce into new, larger ones. In fact, the specific surface area decreases at higher firing temperatures, with a significant fall at 1100 °C (SSA, Table 4).

The addition of fly ash causes few changes in the pore size distribution (Fig. 6). As in the bricks without additives, the displacement of the maximum pore peak is most significant at 1100 °C (r_{max}, Table 4).

The bricks made with coffee grounds are quite different from the others, in that they show a polymodal pore size distribution (Fig. 6). Several families of pores of different sizes form due to the empty spaces left by the burnt coffee particles, although in this case too, the commonest pore size increased in line with the increase in firing temperature, reaching up to 18.2 μm at 1100 °C (r_{max}, Table 4). The appearance of a family of pores at around 0.003 μm in Gfa and Gcg bricks hampers the decrease in SSA at high temperatures (Table 4).

Porosity and density values measured by MIP (P_{oMIP}, ρ_{aMIP}, ρ_{rMIP}) confirm the same tendency of the bricks already described for the hydric tests. The differences are attributed to the use of analytical techniques (MIP and hydric tests) that use liquids with different physical properties and different intrusion pressures.

5.2.3. *Compactness and strength*

The velocity at which ultrasonic waves propagate through the bricks is shown in Table 5. In all the bricks, V_{P1} is always lower than V_{P2} and V_{P3} because the phyllosilicates and rock fragments with planar morphology tend to line up parallel to the compaction plane of the clayey mass when the mix, still moist, is pressed by hand into the wooden mould [41].

Bricks without additives always show the highest V_P values, i.e. greater compactness, reaching an average speed of more than 2500 m/s at 1100 °C. It is interesting to observe how the addition of such different residues as coffee grounds and fly ash, produces almost the same decrease in velocity. Given the higher porosity measured in the bricks with added coffee grounds, one would expect somewhat lower V_P values in Gcg than in Gfa. Indeed, the V_P decrease in Gcg is due to the appearance of new pores after the combustion of this organic residue, already observed under the microscope (Fig. 4) and identified by MIP (Fig. 6). These new pores slow down the movement of the P-waves within the bricks. In the case of fly ash, porosity also increases, but to a lesser extent than with coffee grounds (see P_o and P_{oMIP} values in Table 4), which cannot alone justify a P-wave velocity similar to that measured in Cgc. According to Martínez Martínez et al. [32], this may be due to the presence of large amounts of small fly ash particles in the matrix, which increase dispersion and refraction of the ultrasonic waves as they move, and help slow down the propagation of the waves.

V_P values increase as the firing temperature increases. However, the differences in ultrasonic wave velocity are much more marked between 950 and 1100 °C, in which an increase of about 1000 m/s is registered. This indicates that the sintering and vitrification of the brick matrix take place above all in this temperature range, so confirming the results of the hydric tests.

In general, the structural anisotropy decreases as the firing temperature increases, indicating that the bricks become more isotropic, especially at 1100 °C, due to the gradual vitrification of the samples (ΔM, Table 5).

As regards the mechanical resistance, the increase in the firing temperature makes the bricks more mechanically resistant (CS, Table 5), and the samples follow the same pattern observed with the previous techniques. In other words, the greatest increase in CS is observed between 950 °C and 1100 °C, and the samples fired at the highest temperature are the most resistant, so confirming once again that the bricks undergo substantial vitrification of the matrix in this temperature range. CS also indicates that the firing temperature, especially at 1100 °C which is when the bricks vitrify, has such a strong influence on the results that it masks the presence or absence of residues in the composition. If we compare the bricks with and without additives fired at each temperature, those without additives are the most resistant to the uniaxial compression test, followed by those with fly ash and finally those with coffee grounds. According to the RL-88 [40] standard, only the bricks fired at 1100 °C and those without additives and fired at 950 °C exceed the minimum strength value recommended for bricks for use in building work in Spain. Therefore, the addition of coffee grounds and fly ash would seem to have a deleterious effect on the production of handmade bricks fired below 1100 °C.

If we compare the mechanical strength values for these bricks with those obtained in other studies in which coffee grounds [17,34,49] and fly ash [33] were added, our values were lower, especially at 800 and 950 °C. However, all the bricks used in these previous studies were moulded using a hydraulic press, which, as indicated above, applied a

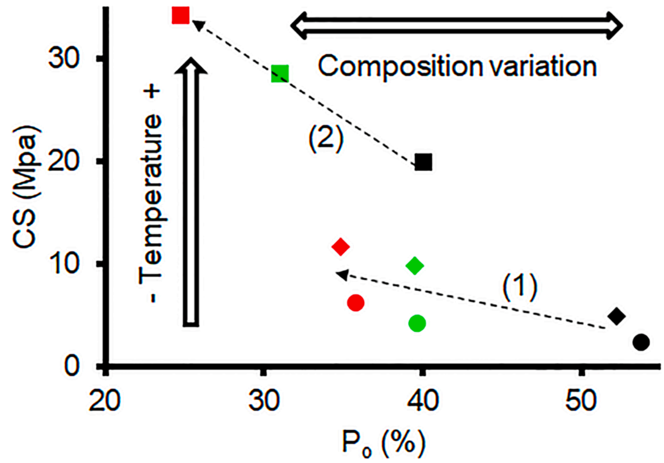

Fig. 7. Correlation between open porosity, as determined by hydric tests (Po, in %), and compressive strength (in MPa). The red symbols represent the bricks with no additives; the green symbols those with added fly ash; the black symbols those with added coffee grounds. The circles represent the bricks fired at 800 °C; the diamonds represent those fired at 950 °C; the squares represent those fired at 1100 °C. Dotted arrow (1) shows the trend of the samples fired at 800 and 950 °C and dotted arrow (2) at 1100 °C.

Table 6
Lightness (L*), chromatic coordinates (a* and b*), chroma (C*) and hue angle (h°) measured in fired bricks without additives (G) and with added coffee grounds (Gcg) or fly ash (Gfa). Each value is the mean of three measurements. ΔE is the colour difference between the bricks with additives and those without additives.

	L*	a*	b*	C*	h°	ΔE
G800	54.05	20.74	28.71	35.42	54.15	
G950	55.61	21.81	27.83	35.37	51.90	
G1100	46.30	19.80	19.19	27.57	44.03	
Gcg800	53.17	20.35	27.77	34.44	53.79	1.83
Gcg950	51.73	22.20	27.57	35.40	51.10	4.40
Gcg1100	47.66	17.72	19.41	27.02	50.22	6.42
Gfa800	56.43	16.68	26.27	31.15	57.72	5.32
Gfa950	61.34	18.17	25.27	31.13	54.31	7.64
Gfa1100	50.75	16.79	20.23	26.41	50.05	7.63

significantly greater load than it is possible to exert by hand, so producing more compact materials. If we compare the hydric and mechanical strength tests, there is a perfect correlation between CS and P_o values. In fact, although ultrasounds measured similar V_P values in bricks with different porosity such as Gcg and Gfa bricks (probably due to the deviation and refraction of the P waves when they moved through a clay matrix that was rich in fly ash), their mechanical strength was unaffected by the presence of ash particles. As can be seen in Fig. 7, as the firing temperature increases, the porosity decreases and the mechanical resistance increases. The composition of the bricks is another important factor, in that regardless of the firing temperature, the bricks made with fly ash or without additives (green and red symbols in Fig. 7) are grouped together with similar values, while those with added coffee grounds (black) appear separately, some way away.

The added porosity in Gcg therefore has a negative effect on the strength of these samples. Another important piece of information can also be gauged from this diagram: at 800 °C and 950 °C, the addition of either coffee grounds or fly ash has a more significant impact on the porosity than on the mechanical resistance of the bricks (see slope of arrow 1); at 1100 °C, the vitrification of the bricks significantly strengthens the bond between the mineral phases and the matrix, thus increasing the mechanical resistance with respect to porosity, regardless of the composition (see slope of arrow 2).

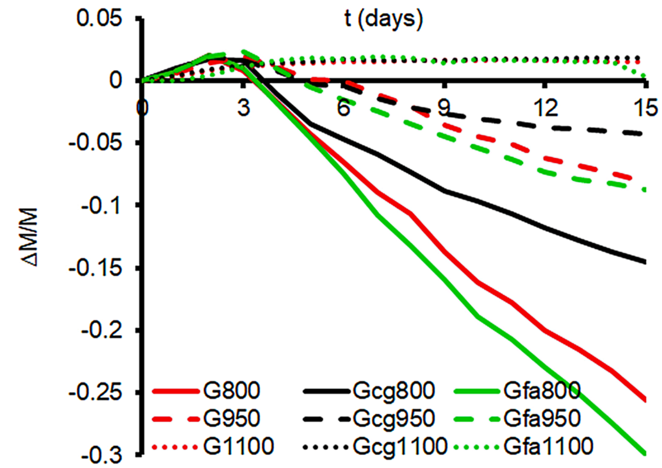

Fig. 8. Weight variation (ΔM/M) in fired bricks made without additives (G) and with added coffee grounds (Cgc) or fly ash (Gfa) over 15 salt crystallization test cycles. Each curve represents the mean of three measurements. Brick acronyms as in Table 1.

5.2.4. Lightness and chromatism

In general, all the samples are red-yellowish in colour due to the iron present in the raw material, which crystallizes in the form of hematite in the fired samples (Tables 2 and 3). Hematite is a mineral phase that pigments the bricks [11]. For each firing temperature, the lightest-coloured samples were those made with fly ash (L*, Table 6). This is because the addition of fly ash causes a whitish patina to develop on the surface of the bricks that can be seen with the naked eye. The composition of this patina was recently described by Saenz et al. [44] and is produced by the deposit of secondary calcite on the surface of the brick. This happens during the immersion of samples in water to prevent "lime blowing" when they are removed from the oven. During immersion, the fly ash particles release the excess calcium they contain, i.e. the calcium that was not involved in the formation of the new silicates, which precipitates as calcite.

If we compare the L* values at the three firing temperatures, the samples fired at 1100 °C always show the lowest values. The lowest value of all was recorded for the G1100 sample (Table 6). These samples are visibly darker than those fired at 800 and 950 °C.

As regards colour, the b* coordinate seems to be most affected by the firing temperature, while a* depends more on the composition of the bricks. If we begin by looking at firing temperature, at 800 and 950 °C, b* ranges approximately between 25 and 28, while at 1100 °C it drops to 19–20. If we focus on composition, bricks without additives and with coffee grounds tend to have higher a* values than those made with fly ash, the samples with the lowest saturation (C*, Table 6).

The colour difference (ΔE, Table 6) between the bricks manufactured without residues and those made with residues shows that the greatest variation in colour occurs in the bricks to which fly ash was added. Furthermore, ΔE increases in line with firing temperature. With the exception of Gcg800, the other samples can be visually distinguished from those that do not contain additives. Gcg950 is in the 3.5 – 5 range, where colour change can be perceived by the human eye. The others have ΔE greater than 5, the threshold beyond which two colours are considered significantly different [31].

5.2.5. Durability

To assess the durability of the samples, an accelerated aging test by salt crystallization was carried out. In this test, the bricks fired at 800 °C suffered the greatest weight loss, followed by those fired at 950 °C, while the weight of those fired at 1100 °C increased slightly at the beginning and then remained almost constant throughout the remainder of the test (Fig. 8). This shows that the firing temperature and, by extension, the

Table 7
Weight loss of bricks with and without additives after 15 salt crystallization test cycles.

G800	G950	G1100	Gcg800	Gcg950	Gcg1100	Gfa800	Gfa950	Gfa1100
0.29	0.10	0	0.17	0.06	0	0.34	0.11	0.01

degree of vitrification play a key role in the durability of bricks. Those fired at 1100 °C are the most durable due to their high level of vitrification. Conversely, the samples fired at 800 °C, which are poorly vitrified, suffer most decay. They gain weight until the third cycle due to the deposition of sodium sulphate in pores and fissures. Then they begin to lose weight due to sanding. This starts from the vertices and edges of the cubic samples, making them more rounded in shape. Sanding also occurs in the samples fired at 950 °C, although in a less pronounced way, while those fired at 1100 °C appear intact at the end of the test. As regards the influence of the residues, the same general pattern is observed: at all three firing temperatures, the samples with added fly ash (Gfa) lose more weight than their counterparts fired at the same temperature, followed by the samples without additives (G). The bricks made with added coffee grounds (Gcg) suffer the lowest weight loss, although at 1100 °C the difference is insignificant with respect to the other two groups of bricks. This means once again that the high level of vitrification reached by all the bricks partially masks the differences in composition. Hydric tests and MIP analysis highlighted that Gcg are the most porous bricks and have the largest pores (P_o and r_{max}, Table 4). This reduces the pressure exerted by the salts when they crystallize inside them [47]. The Gfa1100 brick begins to lose weight at the end of the test, thus confirming that fly ash appears to be the least suitable additive to resist attack by salts. At the end of the test, the samples were washed several times to eliminate the salts present inside the bricks and thus determine the weight loss suffered by the samples after the aging test. Once again, we found that the bricks become more durable as the firing temperature increases, especially when coffee grounds were added to the raw material (Table 7).

6. Conclusions

In this study, the mineralogy, texture, physical–mechanical properties and durability of solid bricks were determined in order to evaluate the advantages and disadvantages of the addition of coffee grounds and fly ash residues to a clayey raw material rich in quartz and phyllosilicates.

The mineralogical changes that take place during firing are directly related to the composition of the raw material and are not influenced by the presence of the residues. The firing of the bricks causes the decomposition of the phyllosilicates, the crystallization of Fe in the form of hematite (responsible for the reddish colour of the bricks) and the appearance of mullite that replaces the dehydroxylated illite/muscovite. Texturally, the addition of coffee grounds leaves imprints where these organic fibres were once present, while the rounded dark spheres of fly ash are distinguishable in the matrix of the bricks. In all the bricks, the matrix gradually becomes less birefringent due to vitrification. This phenomenon occurs mainly from 950 °C to 1100 °C, as demonstrated by the various physical tests conducted. In fact, vitrification reduces the porosity and increases the ultrasonic wave velocity, especially in the 950 °C to 1100 °C temperature range. The bricks become more compact and less anisotropic with greater resistance to mechanical stress. The most significant changes caused by the addition of fly ash and coffee grounds occurred in the porous system. New families of pores appeared and porosity increased, especially in the bricks made with coffee grounds. This enhanced their capacity to absorb water. The bricks made with coffee grounds were less compact and less mechanically resistant, which is a disadvantage if they are to be used in construction. On the other hand, they were also lighter, which could be an advantage when transporting these materials. The development of large pores in the bricks made with coffee grounds makes them more resistant to salt-induced decay. In fact, these bricks proved more durable than those made without residues or with fly ash. Those made with fly ash were the most prone to decay. In future studies, we will assess the degree of thermal insulation that bricks with added coffee grounds could achieve compared to the other two brick types due to their higher porosity levels.

The vitrification process is beneficial for both the physical–mechanical properties and the durability of the bricks, which is why those fired at 1100 °C performed best. According to the Spanish recommendations governing the use of bricks in construction, the bricks that proved suitable for use as construction materials were those fired at 1100 °C, which had a compressive strength of over 10 MPa. The firing temperature and therefore the vitrification are so influential that they mask the effect of the additives on the mechanical behaviour of bricks. However, the bricks made with either residue always achieve lower resistance values than those made without them. While fly ash does not seem to improve the qualities of the bricks and its only clear advantage lies in the savings in the amount of clayey raw materials required, coffee grounds, by contrast, offer various advantages that should be taken into account. First of all, they help save energy by acting as catalysts in the firing process. They also favour the production of lighter bricks (with up to 50% porosity) and they are the most resistant to decay by salt crystallization. This means that, despite their low mechanical resistance, bricks made with coffee grounds could be recommended for use in certain situations due to their highly specific qualities.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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